# A statistical evaluation of the contribution of mineral and tap water to the dietary intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn by humans

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# 1 Introduction

Agriculture is a main contributor to environmental loads of nearly all elements of the periodic system. Not only waste based fertiliser materials like sewage sludge, but also mineral fertilisers and particularly mineral phosphorus fertilisers contain significant amounts of elements which affect the quality of the environment and the food plants.

The Institute of Crop and Soil Science of JKI[1] estimates for the time span from 1950/51 to 2007/2008 the annual average loads of the elements As, B, Cu, Li, Mo, Ni, Pb, U and Zn to agricultural land in Germany exclusively through the application of phosphorus fertilisers to (T/a) As 40 (73), B 1378 (2288), Cu 95 (146), Li 10, Ni 54 (91), Mo 27 (47), Pb 11 (20), U 114 (228) and Zn 431 (764) tons (values in brackets are maxima values). Some of these elements are essential for plants and higher organisms, like B, Cu and Mo, others show a significant toxicity for life processes like As, Pb and U (tab. 1).

Table 1: Occupational limits for heavy metals and their species with some selected toxic substances (from Busby and Schnug 2008)

| | Cd | Cr | As, Co, Hg, Pb | U | Ni, Sb, V | Cu, Zn |
|---|---|---|---|---|---|---|
| Occupational limit (mg/m³ ) | 0.015 | 0.05 | 0.1 | 0.25* | 0.5 | 1.0 |
| Reference-substances | | | Christobalite 0.15 | | Warfarin 0.7; Bromine 0.7 | CaNCN 1.5; $Cl_2$ 1.5; Cyanide 5 |

*NIOSH/OSHA (National Institute for Occupational Safety und Health): Recommended Exposure Limit (REL) and Permissible Exposure Limit (PEL): 0.05 mg/m³ for uranium dust; NRC (Nuclear Regulatory Commission) reports an "occupational limit" of 0.2 mg/m ³; Agency for Toxic Substances and Disease Registry (ATSDR; http://www.atsdr.cdc.gov/ToxProfiles/phs150.html)/
the table addresses only the chemical toxicity and NOT the radiological or combined chemical/radiological one through secondary photon emission damage (Busby and Schnug 2008)

But also those elements which are essential may become toxic in higher concentrations like Cu and Zn. In a recent paper Chandrajith et al. (2010) associate the rising number of chronic kidney disease patients with no identifiable cause (CKD of uncertain aetiology) to increased exposure to uranium and other heavy metals deriving from fertilisers.

[1] Calculated from the official database for consumption of phosphate fertilisers in Germany (Kratz et al. 2011) and element data provided by Kördel et al. (2007) and Senesi et al. (1979).

There are two major pathways through which elements enter the food chain: either through uptake in food and forage plants or through leaching in potable ground and surface water bodies. Transfer Factors (TF) for the elements in question give an idea to which extend these elements may enter the food chain through the soil/plant pathway when applied with fertilisers (tab. 32 in annex).

Table 2: Schematic display of the susceptibility of As, B, Cu, Li, Ni, Mo, Pb, U and Zn to plant uptake and leaching (asssuming an input to soils through fertiliser materials, on basis of data by Akthar et al. 2003, Baes et al. 1984, Ban-Nai et al. 2006, Busby and Schnug 2008, El-Ramady 2008, Förster and Grathwohl 2006, Jaques et al. 2008, Kratz et al. 2011, Ozturk et al. 2004, Scheffer and Schachtschabel 2002, Susset 2009, Tyler 1978; Ni and Cd are shown in the table as a means for a relative comparison; for the soil/plant pathway individual data are given in tab. 36 in annex.)

| **Element** | **Average annual load (t) through P fertilisers** | **Average % of soil background concentration derived from P fertilisation** | **Susceptibility to plant uptake** | **Susceptibility to leaching** |
|---|---|---|---|---|
| N | 112,948 | 7.2* | Very high | Very high |
| B | 1,378 | 4.4 | High | High |
| Zn | 431 | 1.0 | | Medium |
| Cu | 95 | 0.7 | Medium | Low |
| Mo | 27 | 4.6 | | Medium |
| Ni | 54 | 0.5 | Low | Medium |
| Pb | 11 | 0.3 | | Very low |
| As | 40 | 0.9 | | High |
| Li | 10 | -- | | High |
| Cd | 19 | 7.7 | | High |
| U | 114 | 7.8 | Very low | High |

Remark: * percentage of N from NP and NPK-fertilisers from total N fertiliser sale

Compared to this the entry of elements into the food chain through drinking water is much more directly. Ground water resources are prone to anthropogenic contaminations not only depending on their depth in the ground and shielding by low permeable geological bodies, but also by the site dependent leachability of the individual elements, which is mainly affected by

physical, biological and chemical properties of the soils to which fertilisers are applied. Tab.2 displays schematically the susceptibility of As, B, Cu, Li, Ni, Mo, Pb, U and Zn to plant uptake and leaching.

A closer look to the transfer pathways for the elements is of great importance when it comes to a risk assessment through which pathway the elements disposed with fertilisation may enter the human body and which measures should be taken into account to affect the uptake of this elements by humans, either with view to the prevention of loads negatively affecting health or with the objective to compensate for an even more health affecting deficiency of an essential micro nutrient.

Finally, for a correct assessment of risks arising from dispersing elements with fertilisers it is necessary to know to which extend which of the two general pathways, solid or liquid food contributes to the total daily intake. This information is especially necessary to assess efficient abatement strategies for contaminations in the food chain.

The main objective of the research work presented here was a statistical evaluation of the contribution of mineral and tap water to the dietary intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn by humans in order to identify potential hazards from contaminations with these elements through fertilisfer use in agriculture.

The background for such a comparison would be the amount of this element taken in daily through solid foods. A prime source for such data is the data bases of EFSA (European Food Saftey Agency), which rely on reports of the member countries of the European Union. However, these data show a very large inexplicable variability, which hampers a bias free comparison of individual diet strategies or drinking habits. Therefore, part of the research work presented here was also the development of standardized diet types as bias free data background for the human exposure to As, B, Cu, Li, Mo, Ni, Pb, U and Zn through solid food.

## 2 Significance of As, B, Cu, Li, Mo, Ni, Pb, U and Zn for human health

Elements exist naturally in our environment, they occur naturally in the earth's crust, where some elements such as Pb and Zn are widely distributed. Elements spread into the air, soil and water (lake, oceans, surface and ground water and drinking water) by means of two processes: natural process such as volcanoes and by man-made activities such as industrial activities like mining, smelting, coal burning and during smelting process of various metal ores, the second process represent the major way of Ni and Zn spreading into the environment. Element concentrations in different environmental components are variable: As for example occurs in trace amounts in soil, water and air, whereas B concentration is about 30 mg/kg and 0.5 mg/L in soil and surface water respectively, but they are about 4 - 80 mg/kg of soil and 10 mg/L of surface water for Ni. Element concentrations in the air present in trace amount in the case of As, low in Cu, and relatively high 0.03 μg/$m^3$ for Mo. Humans are primary exposed to elements through diet, drinking water, air, and dust. As is considered as a toxic metalloid, whereas most other elements are essential for human nutrition such as B, Cu, Mo, and Zn, so their presence in the human diet is recommended in low concentrations, but when they present in high concentration they become toxic. Food and drinking water represent the main sources of elements for human being, the measured concentration of B in drinking water is between 0.1 - 0.3 mg/L, whereas it is 20 - 75 μg/L for Cu, and 2 - 4.3 μg/L for Ni. The recommended limit concentration in drinking water is different with organizations dealing environment, but generally 0.01, 1.3, 0.7, 0.07, 0.01 and 5 mg/L are the limited concentrations of As, Cu, Li, Mo, Pb and Zn respectively. The daily intake from food and drinking water is also variable with elements, the estimated intakes are 2, 1.2, 1.13, 0.152, 0.168 mg/day for Li, B, Cu, Ni and Pb respectively, and the recommended daily intake of Mo is 75 - 250 μg/day and 15 - 22 mg/day for Zn. The occupational exposure of workers in the workplaces may be exposed to higher levels of elements than the general public.Exposure to hazardous elements may cause a few symptoms such as fatigue, skin and eye irritations, decreased appetite, weakness, headache, anorexia, arthralgia, chest pain, cough, diarrhoea, and myalgia. As human carcinogens, As is classified human carcinogens, Ni as a possible carcinogen but nickel compounds are considered as human carcinogens, but all the other elements are not classified carcinogens for human.

Specific features for each of the nine elements covered by this research work will be discussed in details below.

## 2.1 Arsenic

Arsenic is a natural element and widely distributed in the earth's crust and soils (ATSDR 1998). It is an odourless and tasteless semi-metal; it is known as metalloid and grouped as a toxic metal (Dartmouth Toxic Metal Research 2001). It is classified as the most hazardous between twentieth hazardous substances (Goering et al. 1999). Two general types of As compounds occur in the environment, inorganic and organic form. In inorganic forms As combines with other elements such as oxygen, chlorine and sulphur (ATSDR 1998). But when it combines with carbon and hydrogen in organic forms, these compounds are used as pesticides in agriculture mainly in cotton fields, and they accumulate in seafood, like fish and shellfish. Animal studies reported that some organic As compounds are less toxic than inorganic ones (ATSDR 2007a). As exists as trace amounts in oceans, soil, water, air and food (Dartmouth Toxic Metal Research 2001, Green Facts 2004a). Its average content for instance in rock or soil is 2 mg/kg (Dartmouth Toxic Metal Research 2001). Inorganic As comes in the atmosphere from two sources: either from natural processes such as volcanoes, or from man-made sources such as industrial activities like mining, smelting, where As is released from coal burning and during smelting process of various metal ores such as Cu, Pb, Zn, Co, Au, and Ni in which As is present as a byproduct (Green Facts 2004a). It comes also by commercial processes, and by weathering As-containing minerals and ores (ATSDR 1998). Inorganic As compounds are used in glass and ceramic industries and also in wood preservation products (HPA 2007). Organic compounds are used as pesticides in agriculture mainly in cotton fields and they accumulate in seafood, like fish and shellfish. They cause less harm to health than the inorganic form (RAIS 2005a). In the $19^{th}$ century, As compounds were used in human medicine to treat some diseases such as skin, syphilis and digestive problems. Later it has been noticed that some of these medicines could develop cancer at the skin sites where the drug was applied. Between 1940's and 1950's most of the medical products containing As were suspended, nevertheless one of these products called Melarsoprol is still in use for African sleeping sickness treatments, and other organic compounds are still in use in medicine (Dartmouth Toxic Metal Research 2001, Roy and Saha, 2002). Because of their low As content, foods are not a major source of As toxicity for human health, it presents in extremely small concentration in vegetables and fruits, but the concentration of As in some aquatic animals is slightly higher such as fish and shellfish (Dartmouth Toxic Metal Research 2001). Presence of As in drinking water has more concern for human health than in foods. The U.S EPA has determined a limit of 0.01 mg/L for As in

drinking water (ATSDR 2007a). Several epidemiological studies have shown that As concentrations in drinking water can increase the risk of skin, liver, and bladder cancers as well as respiratory and gastrointestinal tracts (RAIS 2005a). These concentrations must be less than 0.05 mg/l, and the principal human health concern from As is skin and internal cancer (WHO 2001a), as well as the exposure to As in drinking water becomes a health concern in the United States because of the high levels of As in its bedrock (Dartmouth Toxic Metal Research 2001). Cancer of skin, lungs, bladder and kidneys are caused by long exposure to As content in drinking water (WHO 2001a). Exposure to As occurs in two ways: acute and chronic exposures. Acute exposure is a large dose in a short period of time and it produces immediate effects, while chronic exposure is a lower dose of As over a longer period of time that produces a gradual delay effects (Dartmouth Toxic Metal Research 2001).

1 - Arsenic exposure: the chronic exposure to As can cause weakness, lassitude, general debility, loss of hair, loss of appetite, loss of energy and weight, hoarseness of voice, and mental disorders (RAIS 2005a), and it causes disorder of central and peripheral nervous system (ATSDR 1998). The main target of As is skin, vascular system, and nervous system. While the main effects of acute inhalation exposure to high levels of As are gastrointestinal effects; these effects include nausea, diarrhoea, and abdominal pain (ATSDR 1998). The acute lethal dose to human is about 0.6 mg/kg/day (RAIS 2005a). Damage of ingesting exposure to As depend on its level, it could cause death when it is high, but it can result in nausea and vomiting, damage to blood vessels, decrease of red and white blood cells, abnormal heart rhythm (ATSDR 2007a).

2 - Inorganic arsenic exposure: the chronic inhalation exposure to inorganic As causes irritation of the skin and mucous membranes (ATSDR 1998). Although chronic oral exposure of human to inorganic As can cause gastrointestinal effects, skin lesions, anaemia, peripheral neuropathy, liver or kidney damage and vascular lesions (ATSDR 1998, ATSDR 1990a). While acute exposure to inorganic As causes nausea, anorexia, vomiting, abdominal pain and diarrhoea (RAIS 2005a), and acute oral exposure of human to high levels $\geq$ 600 μg/kg/d of inorganic As can cause death, whereas exposure to lower doses causes nausea, vomiting, headaches, weakness, delirium, liver, kidney, and blood effects (ATSDR 1998, ATSDR 1990a). As well as inhalation or ingestion of low doses of inorganic As over a long period of time can cause small warts on the sole and palms and a darkening of the skin (ATSDR 2007a). Many studies have reported a relationship between ingestion of inorganic As and increase the risk of skin, lung, liver, kidney, bladder, and prostate cancer (RAIS 2005a, ATSDR 2007d). Also several studies have shown the association between inhalation

inorganic As and lung cancer (ATSDR 1998, ATSDR 1990a). Finally, As is classified by the Agency for Toxic Substances and Disease Registry (ATSDR) and the United States Environmental Protection Agency (U.S. EPA) as the most hazardous between twentieth hazardous substances (Goering et al. 1999).

Many organizations such as the Department of Health and Human Services (DHHS), International Agency for Research on Cancer (IARC), and the U.S. Environmental Protection Agency (U.S. EPA) have classified inorganic As compounds as carcinogenic to humans (ATSDR 2007d).

## 2.2 Boron

Boron is a trace element essential for plants and may be for humans and animals. It is a naturally occurring element, it combines with O and other substances in the environment to form compounds called borates (ATSDR 2007e). These compounds are present in oceans, coal, sedimentary rocks and some soils (Green Facts, 2004b). These natural sources release B into air, water, or soils (ATSDR 2007e). Human activities contribute in providing B to the environment. These activities include agricultural activities such as using fertilisers and herbicides containing borates (ATSDR 2007e). Human industrial activities also add B to the environment such as borate mining, glass and ceramic manufactures, leather tanning, photographic materials, cosmetics products, laundry products containing B (Green Facts 2004b). The average B concentration in soil is approximately 30 mg/kg, but it is about 4.5 mg/L in oceans, and less than 0.6 mg/L in surface water, whereas the mean concentration of B in drinking water is estimated to be between 0.1 and 0.3 mg/L, whereas very small amounts occur in groundwater (Green Facts 2004b). The main human exposing to B is from drinking water and also from the diet, where the richest sources of B, fruits, vegetables, pulses, legumes, and nuts are included (ATSDR 2007e). The daily B intake via the diet is estimated at 1.2 mg/day per person (Green Facts 2004b). As well as the workers in boron mining and industries containing borates are exposed to B (Green Facts 2004b). Most of the borate and boric acid in both human and animal bodies are absorbed from the gastrointestinal and respiratory tracts and rapidly excreted in the urine (Green Facts 2004b). Regarding B effects on human health, several animal studies indicated that ingestion of large amounts, which represent 1800 time higher than the daily B intake from food by the adults in the United States, affect the male animal's reproductive organs, mainly the testis and affect the

development of the foetus (ATSDR 2007e). Researches demonstrate that exposure to high levels of B (30 g of boric acid) over short period of time can affect and damage the stomach, liver, kidney, intestines, testis, and brain, and can finally lead to death. While workers in boron mining and others workplaces reported nose, throat and eyes irritation (ATSDR 2007e). The same symptoms were noticed by few studies on humans when exposure to B was for short period of time, but these symptoms disappeared when this short-term B exposure stopped (Green Facts 2004b). Two human studies reported that exposure to B had no effects on human fertility (Green Facts 2004b). There are no human studies available about B as carcinogenic, but one animal study reported that cancer occurred after a lifetime exposure to boric acid in food. Because of the limited animal studies and the lack of human data, DHHS, IARC, and U.S. EPA have classified B as no carcinogenic to humans (ATSDR 2007e).

## 2.3 Copper

Copper is a reddish metal classified the third consumed metal after steel and aluminum (Dartmouth Toxic Metal Research 2001). Cu is mainly used as metal or as mixture with other metals, called alloys. These alloys are used in electrical wires and some water pipes manufactures and other metal products. Cu is mostly used to make the U.S. pennies and metal sheet (ATSDR 2004a). Cu compounds are widely used for many industrial applications (ACGIH 1986). Several industrial operations such as smelters, power stations release high levels of Cu to the surrounding air and soil (Dartmouth Toxic Metal Research 2001). The industry of electrical products is considered the next largest consumer of Cu after building constructions, as well as it is used in car and airplanes manufactures (Dartmouth Toxic Metal Research 2001). Cu is used as well in agriculture to treat some plant diseases, and in water treatment (ATSDR 2004a, RAIS 2005b).Cu spreads widely in the environment through natural phenomena, in other words it occurs naturally in rocks, soil, water, and in all plants and animals food resources, and beverages we drink, including drinking water (ATSDR 2004a). The concentration of Cu in the earth crust is about 50 mg/kg, whereas its concentration in the air is quite low (ATSDR 2004a).

The natural concentration of Cu in ground water and surface water is very low, it is about 4 µg/L (Wisconsin Department of Natural Resources 2003). Cu range in tap water is between 20 and 75 ppb, whereas its concentration in lakes and rivers is about 10 ppb (ATSDR 2004a).Cu is an essential trace element in low concentrations for human nutrition, and it is

present in various tissues such as kidney, spleen, liver, lung, heart, muscle, stomach, intestine, hair and nails (U.S. EPA 1987, ATSDR 1990b), while it has toxic effects at higher concentrations (ATSDR 2004b). Human take Cu by drinking water, food, air and through skin contact with soil, but drinking water is considered as the greatest source of Cu. On the other hand U.S. Environmental Protection Agency has established that the concentration of Cu in drinking water should not exceed 1.3 mg/l. Also the U.S. Food and Drug Administration (FDA) has recommended the allowable level of Cu in bottled water of 1.0 mg/L (ATSDR 2004b). The daily intake of Cu from food was estimated between 1.0 - 1.3 mg/day for adults, which corresponded to 0.014 - 0.019 mg/kg/day (ATSDR 2004b).The daily recommended intake of Cu is different between the organizations, for instance U.S. AF (1990) recommended safe dietary of Cu intake of 0.4 - 0.7 mg/day for infants, 0.7 - 2.5 mg/day for children and adolescents, and 1.5 - 3.0 mg/day for adults, whereas the Food and Nutrition Board of the Institute of Medicine has determined the recommended dietary allowance of 900 µg/day for adults. People can be exposed to increased levels of Cu in drinking water as a result of the corrosion of plumbing materials (U.S. EPA 1987), these high levels of Cu and Cu salts in drinking water which exceeds the normal levels may cause gastrointestinal, hepatic and renal effects such as severe abdominal pain, vomiting, nausea, diarrhoea stomach cramp, haemolysis, coma and death (ATSD, 2004, U.S. AF 1990). Accumulation of Cu in tissues can cause a genetic disorder and Wilson's disease, they are considered as chronic toxicity effects of Cu (Goyer 1991, U.S. EPA 1987). Acute inhalation exposure to dust containing Cu or to fumes can cause nausea, headaches and diarrhoea, and it can irritate eyes, nose and mouth (ATSDR 2004b). If the inhaled Cu salts reach the gastrointestinal tract, they may cause increased salivation, vomiting, nausea, diarrhoea, gastric pain, and hemorrhagic gastritis (ACGIH 1986). Children can also be exposed to Cu by skin contact through eating the contaminated dust and touch hand to mouth (ATSDR 2004b).The occupational exposure to Cu dust or fumes for short-term can irritate the eyes and the respiratory tract, and may cause headaches, drowsiness, vertigo, cough, muscle ache and chills (U.S. AF 1990), other effects include metallic or sweet taste and discoloration of the skin and hair (ATSDR 1990b). Workers in Cu mining and in industries of processing the ore or in the work places are exposed to Cu by inhalation or by skin contact (ATSDR 2004b). In factories, where workers sieved Cu dust, they suffered from nausea, anorexia, headache, vertigo, vomiting, and drowsiness (Suciu et al. 1981).In humans, Cu absorbed mainly from the upper portion of the gastrointestinal tract, the lung, and skin into the systemic circulation (U.S. EPA 1987). About 80 % of the absorbed Cu is excreted in the bile, because the biliary system is the major

pathway of Cu excretion, and only 2 - 4% of the absorbed Cu is excreted in the urine (Venugobal and Luckey 1978). U.S. EPA does not classify Cu as a human carcinogen. It is not known if Cu can cause cancer in humans (ATSDR 2004b).

## 2.4 Lithium

Lithium is a trace alkali metal element (Arena 1986). It does not occur naturally in its free form, but its compounds occur in natural water and some foods (Berliles 1994). It is a prevalent element found in humans, animals, and plants in trace amounts (Usuda et al. 2007). Li exists in the earth crust; it is present in trace amounts in soils and plants, and its concentrations range from 8 to 40 ppm and from 20 ppb to 0.3 ppm respectively (Edward et al. 1985). Li salts such as Li carbonate or Li citrate are used extensively in medicine to treat manic-depressive disorder, bipolar disorder (Ellenhorn and Barceloux 1988, Hardman et al. 1996). Elemental Li is used in metal alloys; but Li hydride is considered as nuclear reactor coolant, Li borate and Li carbonate are used in ceramic industry, and Li hydroxide is used in alkaline storage batteries (Berliles 1994).Worldwide, Li concentrations in mineral water range between 0.05 and 1 mg/L, Aral and Vecchio-Sadus (2008) reported that the concentration of Li in rivers water is 3 µg/L, whereas Schrauzer (2002) reported that surface water contains Li at concentrations between 1 - 10 µg/L, and 0.18 µg/L in sea water, while in ground water; these concentrations may reach 500 µg/L. The U.S. EPA's recommendation of Li concentration in drinking water is less than 700 µg/l (Usuda et al. 2007). There is little information about Li compounds toxicity (RAIS 1995). Aral and Vecchio-Sadus (2008) consider Li as low toxicant to human and environment. The average daily intake of Li from food and water is estimated 2 mg (Edward et al. 1985), and in 1985 the U.S. EPA reported a daily intake for a 70 kg adult is between 0.65 and 3.1 mg of Li/day, and the main sources of this dietary are vegetables and grains (Schrauzer 2002). The main target of Li toxicity is the nervous system and its effects occur during the prolonged therapy with Li (Kocsis et al. 1993). These effects include tremor of hands and maybe lips and jaws (OEHHA 2003). Doses of 171 - 857 mg/kg/day for 70 kg person can cause respiratory and cardiac complication, coma, and death (Gosselin et al. 1984). The standard dose of Li carbonate for chronic therapy is 14 - 28 mg/kg/day (Marcus 1980). Severe Li neurotoxicity may occur during chronic therapy such as paralysis, incoherence, stupor, coma, and seizure (Hall et al. 1979). After a long-term of Li therapy, several patients had a permanent brain damage (Gosselin et al. 1984).

Soluble Li compounds are readily absorbed by the gastrointestinal tract and poorly absorbed across the skin (Jaeger et al. 1985), but dermal contact with Li hydride may cause chemical burns (ACGIH 1991). Li is distributed rapidly to kidneys and liver and in a slower extent to other organs (Jaeger et al. 1985). But over 90% of the Li intake by human bodies can be eliminated via kidneys (Usuda et al. 2007). The adverse effects on the gastrointestinal tract are nausea, vomiting, abdominal pain and diarrhoea (OEHHA 2003), other symptoms of Li toxicity are anorexia, thirst, weight gain, acne, anaemia, tremors, alopecia, pretibial oedema, glycosuria, aplastic, and polyuri (Arena 1986). Li can cross the placenta of pregnant, and infants can take it up through breast milk (ACGIH 1991). Few studies have reported that pregnant women on Li therapy may have a higher risk of premature births. And those women, who received Li during early pregnancy, have a risk of getting congenital malformations slightly higher than those women in control groups (Cohen et al. 1994). Little information on the toxicity of Li compounds inhalation is available. The exposure of workers in the occupational places can cause severe nasal, eye, and skin irritation, and respiratory tract irritation were noticed by Li hydride (Beliles 1994). Finally Li is not classified as carcinogenic to humans by U.S. EPA (RAIS 1995).

## 2.5 Molybdenum

Molybdenum is a silver-white colour (Reilly 2002). It does not exist naturally in the pure metallic form, so it occurs in association with other elements (Barceloux 1999). Mo concentrations in the ambient air are lower than other elements concentrations such as Cu, Zn, and Pb (Barceloux 1999). The Mo level in urban air is 0.01 - 0.03 μg $m^{-3}$ (Friberg and Lener 1986) while these levels are 0.001 - 0.0032 μg $m^{-3}$ in rural air (Barceloux 1999). But its concentrations in soil range between 1 - 2 mg/kg (Barceloux 1999). Anthropogenic Mo sources derive from industrial or molybdenum mining operations, coal combustion, and municipal sewage sludge (Barceloux, 1999). Although Mo is widely occurring in nature in various ores and its compounds are mainly used in the metal alloys production (NRC 1989), as well as in chemicals, pigments and ceramic. Metallic Mo is used in induction heating elements, electrodes, and electronic parts (Stokinger 1981).The maximum recommended level of Mo in drinking water is 0.07 mg/L (WHO 1993), whereas Mo concentration in most natural waters is 2 - 3 μg/L (Barceloux 1999). But Mo concentration is 0.2 - 0.4 mg/L in surface water and it may reach up to 25 mg/L in groundwater located near industrial areas and Mo mining (Barceloux 1999). Mo is an essential trace element for human beings and

mammals, because it is required for the function of the enzymes xanthine oxidase, aldehyde oxidase and sulphide oxidase (Rajagopalan 1988, Underwood 1981). On the other side Mo is a toxic element at high amounts (Rajagopalan 1988). Its toxicity depends on its physical and chemical forms, and insoluble compounds are less toxic than soluble ones. In humans, a low order of toxicity of Mo compounds has been reported, and there are no records about lethal doses (Vyskočil and Viau 1999).The main source of Mo in the human body is diet, while its daily intake from drinking water and from air is negligible (Lener and Bibr 1984). It is not known the minimum dietary requirement of human from Mo (Rajagopalan 1988), and the provisional recommended dietary intake of Mo for adults is 75 - 250 µg/day (NRC 1989), but Leichtmann and Sitrin (1991) reported that the estimated adequate and safe range of Mo for adults is 150 - 500 µg/day, whereas the WHO determine the daily requirement of Mo for adults from 0.1 to 0.3 mg/day (WHO 1993). An association was noticed between Mo toxicity and Cu intake, where humans who have dysfunction in Cu metabolism or Cu deficiency because of inadequate Cu intake, may be exposed to higher risk of Mo toxicity (ACGHI 1991). The absorption of Mo in the human body is determined by its chemical form and also the way of exposure. Water-soluble Mo compounds as well as sparingly soluble compounds such as Mo trioxide and calcium molybdate are readily absorbed through the gastrointestinal tract (RAIS 2005). As well as the lungs absorb only water-soluble compounds, but not insoluble compounds (Friberg and Lener 1986). And more than 80 % of ingested Mo from food is absorbed in the stomach and the remainder in the small intestine (Reilly 2002). The highest concentrations of the distributed Mo throughout the human body are in the kidneys, liver, spleen, and bones (Wennig and Kirsch 1988). Mo has a preference to deposit in fat tissues such as brain which is rich in fat tissue (Sullivan and Krieger 1992). Mo is mainly excreted in the urine, where the urinary excretion is 17 – 80 % of the absorbed amount, and only small amounts are excreted via the bile (Vyskočil and Viau 1999).Inhalation of metallic Mo and soluble compounds (e.g. Mo disulphide, metal, dioxide) have been damaged the lungs and caused pneumoconiosis (occupational lung disease) in few cases (Vyskočil and Viau 1999). Chronic Mo exposure may be cause a few symptoms such as fatigue, listlessness, decreased appetite, weakness, headache, anorexia, arthralgia, chest pain, cough, diarrhea, and myalgia. But acute Mo toxicity may affect male gonads and causes testicular atrophy (Lesser and Weiss 1995). Occupational exposure of workers in Cu-Mo plants can cause gout-like and increased blood uric acid concentrations, as well as the general public living in areas with high Cu and Mo levels in soil and vegetables may observe the same symptoms (Vyskočil and Viau 1999). Some symptoms of Mo exposure were determined by the occupational exposure

studies and were observed in Russian workers in Mo processing plant and Mo mine, these symptoms were fatigue, weight loss, weakness, irritability, sweating, epigastric pain, lack of appetite, headache, dizziness, joint and muscle pain, and tremor of the hands. And a number of symptoms were reported in American workers at a U.S. Mo-roasting plant such as backaches, joint pain and non-specific hair and skin changes (RAIS, 2005). There is no evidence of carcinogenicity of Mo. US Environmental Protection Agency and the American Conference of Governmental Industrial Hygienists (ACGIH) has not been reported Mo as a human carcinogen (ACGIH 1998).

## 2.6 Nickel

Nickel is a hard silvery-white metal. It combines with S, O and Cl to form green coloured compounds, Ni combines also with other metals such as Fe, Cu, Cr, and Zn to form alloys (ATSDR 2005a). Ni occurs naturally in the earth's crust, soil and rocks. It is found in various environmental media such as lakes, rivers, oceans, drinking water and air (U.S. AF 1990). Forest fires, windblown dust, vegetation and volcanoes represent natural sources of Ni in the environment (ATSDR 2005a, HPA 2009). Records of Ni concentrations in ambient air ranged between 7 and 12 ng/m³ in the United States between 1977 and 1982, but lower concentrations about 2.2 ng/m³ were estimated by the U.S. EPA in 1996 (ATSDR 2005a). While the concentrations of Ni in soil vary widely and ranged between 4 and 80 mg/kg (ATSDR 2005a). Ni compounds are primarily used in nickel-cadmium batteries, electroplating, ceramics and pigments, and it is widely used in metallurgical processes like in stainless steel production. Other alloys are used to produce electrical equipment, household cookware, jewellery, and coins (Goyer 1991). Ni can be released into the environment mainly through human activities such as production of steel and other Ni alloys, oil and coal combustion, electroplating and Ni refining (IPCS 1991, ATSDR 2005a). The Ni concentration in water (lakes, rivers) is very low, it is less than 10 ppm. The concentrations of Ni in drinking water ranged from 2 to 4.3 ppb in the United States. Highest concentrations of Ni, 72 ppb in drinking water were found in areas near Ni mining and Ni refinement. U.S. EPA has recommended that the Ni concentration in drinking water should not exceed 0.1 mg/l (ATSDR 2005a). The biggest sources of Ni exposure for humans is from ingesting contaminated food and from cigarette smoking (WHO 2000b). The approximately adult daily intake from food has been estimated about 152 microgram of Ni (DEFRA and EA 2002). The general population can be exposed to low levels of Ni through ingestion drinking water

contaminated with Ni or by inhalation of Ni contaminated air (ATSDR 2005a). People may also be exposed to trace amounts of Ni by skin contact with products that contain Ni such as coins and jewellery (HPA 2009). Based on the above average of Ni concentrations in drinking water, and the assumption of 2 L/day of water consumption, the estimated daily intake of Ni in the U.S. ranges between 4 and 8.6 μg/day from drinking water. Based on water and food content, and assuming 70 kg of body weight, the range of Ni intake from food can be estimated 69 - 162 μg/day, and the total daily dose between 0.001 and 0.0024 mg/kg/day for adults (ATSDR 2005a). The occupational exposure of workers in workplaces to Ni or its compounds can occur in industries that use process or produce Ni, and they may be exposed to higher levels of Ni than the general public (ATSDR 2005a). Those individuals may be exposed to Ni from inhalation of Ni carbonyl gaseous, or inhalation of mists, fumes, and dusts that contain Ni, or by skin contact with Ni (IARC 1990). Ni is primarily absorbed from respiratory tract. The absorption extent of Ni after inhalation depends on its particle size, density, shape, and electrical charge (ATSDR 1988), and also depends on Ni compound solubility, where smaller compounds are readily absorbed, and therefore can penetrate deeper into the lungs (IPCS, 1991). Ni is poorly absorbed from the gastrointestinal tract (Coogan et al. 1989). But some Ni compounds such as Ni sulfate and Ni chloride can be absorbed from occluded skin but metallic Ni is poorly absorbed from skin (ATSDR 1988). Exposure of workers in electroplating plant to Ni chloride and Ni sulfate from contaminated drinking water caused abdominal pain, diarrhea, vomiting, nausea, headache, cough, giddiness, and shortness of breath (Sunderman et al. 1988). Increased risks of lung and nasal passages cancer and chromosome aberrations have been reported in individual workers involved in electroplating, smelting, crushing, and roasting processes of Ni (IPCS 1991, Magnus et al. 1980). While no significant increase in respiratory tract cancer between workers involved in Ni alloys manufacture (IARC 1990), but increase of irritation in airway and eyes, tiredness and headaches has been recorded (Akesson and Skervfing 1985). There are limited data available on human effects from acute inhalation of elemental Ni (ATSDR 2005a). As well as the available data on the acute human effects of Ni salts ingestions are limited. The most toxic Ni compound is Ni carbonyl. A lot of immediate and delayed symptoms can occur following acute exposure to Ni carbonyl (IPCS 1991). The immediate symptoms include respiratory tract irritation and neurological symptoms such as headache, vomiting, dizziness, nausea, upper airway irritation and irritability (Shi 1994, DEFRA and EA 2002). The other toxic and delayed effects may be occurring in the following stage of acute exposure to Ni carbonyl include tachycardia, chest pain, cough, weakness and fever. The severe exposure to Ni

carbonyl may cause pulmonary haemorrhage, pneumonitis, cerebral oedema and neurasthenic syndrome (IPCS 1991, Shi 1994). Regarding health effects of chronic exposure to Ni and its compounds. Major effect of toxicity of inhalation of Ni and Ni compounds is the respiratory tract. The occupational exposure of individuals to Ni dusts or Ni compounds can frequently cause respiratory disorders such as asthma, sinusitis, hyposmia, anosmia, rhinitis, emphysema and chronic bronchitis (IPCS 1991, USAF 1990). On the other hand the dermal exposure to Ni or water soluble Ni salts may cause outbreaks of dermatitis (IPCS 1991). The distribution of Ni through the human body affected by the chemical form, time elapsed after exposure, and the route of exposure (Coogan et al. 1989). Ni mainly accumulates in kidneys and lungs, while liver, heart, and spleen are also other organs of accumulation of metallic Ni but in lesser extend. Excretion of Ni occurs through the urine and faeces, mostly through faeces. Ni may also be eliminated in the sweat and hair (ATSDR 1988). Finally, the International Agency for the Research on Cancer (IARC) classified elemental Ni as a possible human carcinogen (Group 2B), but Ni compounds are classified as human carcinogens (Group 1) (IARC 1990). Whereas U.S. EPA has determined Ni subsulfide and Ni refinery dust as human carcinogens (U.S. EPA 2000).

## 2.7 Lead

Lead is one of the most common heavy elements interfering with environmental quality. Pb is a bluish-gray malleable metal and usually found combined with other elements to form lead compounds but rarely found as a metal, it is found naturally as a sulfide in the earth's crust in galena (ATSDR 2007b). Pb is widely distributed in air, water, soil and rocks. The inorganic forms of Pb are a result of combustion of leaded petrol, and most of the emitted Pb into the atmosphere is in an inorganic salt (HPA 2007). Pb concentrations in soils vary widely, it is about 3000 µg/g in urban areas, but it does not exceed 30 µg/g in rural areas (RAIS 1994). The U.S. EPA recommended that the concentration of Pb in air should not exceed 1.5 $\mu g/m^3$ "as average for more than three months" (ATSDR 2007c). The overall occurrence of Pb in the environmental media is a result of anthropogenic sources, such as industrial emissions from Pb and other metals mining, recycling, smelting or waste incineration (ATSDR 2005d; DEFRA and EA 2002). In soil, Pb is mainly coming from solid wastes, sludge, sewage and other industrial sources (DEFRA and EA 2002), paint containing Pb is another source of Pb specially in old houses inside cities, whereas Pb is coming into the air from coal burning, oil,

or solid waste, or from fumes and exhausted from gasoline containing Pb, and from cigarette smoke (ATSDR 2007c). For these reasons the use of Pb in petrol, paint and pipes has been phased out and the U.S. EPA has banned the use of Pb in gasoline for motor vehicles, these procedures leads to decrease of Pb concentration in the air (ATSDR 2007c). Pb compounds are used also in paints, dyes, and ceramic glazes. In recent years the amount of Pb in these products has been reduced to minimize the health effects of Pb on humans (ATSDR 2007b, c). Metallic Pb and Pb alloys are used widely in manufactures such as plumbing and in storage batteries used largely in cars and various vehicles, solders and steel product pipes, weights, cable covers, and in bullets, shot and ammunition. Inorganic Pb salts are used in paints, pigments, insecticides, ceramics, and plastic and rubber products and as a part of glazing for pottery (ATSDR 2007b, HPA 2007). Pb in water and soil may result from industrial activities. Pb can leach from water systems which have old lead pipes or lead solder that use for Cu pipes (DEFRA and EA 2002). Pb may come to soil and surface water from small Pb particles which travel long distance, and fall down then removed from the air by rain. Generally Pb levels in rivers, lakes are very little as well as in the groundwater which used as public supplied for drinking water (ATSDR 2007b). The average Pb levels in surface water are 3.9 μg/L and 0.005 μg/L in sea water (RAIS 1994). The WHO reported that the permissible limit of Pb in water is 0.01 mg/L (WHO 1997). The primary route of Pb exposure is through ingestion or inhalation, and exposure to Pb by soil, dust, air, and paint chips contributes to the whole exposure (IPCS 1995). Therefore, most people are exposed to Pb or its compounds through drinking water, eating food or swallowing airborne dust or dirt that contain Pb. In addition, by breathing contaminated air like exhaust fumes (ATSDR 2007c, HPA 2007). As well as the main exposures of children to Pb are flaking paint, paint chips, powdered paint or by hand-to-mouth contact from contaminated soil with Pb (ATSDR 2007c, HPA 2007). Otherwise, people who are living in or near old houses which have been painted with Pb paint, or near hazardous waste sites, or near busy highways may be exposed to higher levels of Pb and its chemical forms (ATSDR 2007c). Workers in occupational places may also be exposed to Pb by breathing the contaminated air with Pb particles and its compounds used in these occupations such as steel welding, smelting and refining industries, soldering, rubber products and plastic industries, pottery and ceramic industries, battery manufacturing, plumbing and paint removal associated with building renovation, these workers may bring Pb dusts with their work clothes to their homes and families (ATSDR 2007c). As mentioned above humans may be exposed to Pb primarily through diet, drinking water, air, and dust. In contrast, in occupational places, the main route of human's exposure to inorganic Pb is

inhalation of mists, fumes, and vapors (ATSDR 2005d). The daily Pb intake from foods is $2.8 \times 10^{-2}$ mg (Santos et al. 2004). And the daily Pb intake range reported in the literature are between 0.007 and 0.23 mg/day (Santos et al. 2004). Whereas the WHO reported that the daily intake of Pb is 0.25 mg/day for a 70 kg adult (WHO 1993). The adverse human health effects depend on the way, amount (dose) and duration of exposure, and chemical forms of the element (HPA 2007). Generally, no health effects should occur from foods, drinking water or inhalation of contaminated air for a short time. But exposure to Pb or Pb compounds over a long period of time can cause headache, nausea, vomiting, lethargy, anaemia, irritably, high blood pressure, or kidney or liver damage (HPA 2007). The U.S. EPA reported a positive relationship between blood pressure and blood Pb levels in middle-age for men (RAIS 2005), so the Pb exposure can be measured by the concentrations of Pb in blood (PbB) and therefore the effects of Pb are described by PbB concentrations (RAIS 1994). Pb is a cumulative or chronic toxin. Exposures of Pb, acute or chronic, affect human health. The acute effects include neurological effects such as encephalopathy, drowsiness, malaise, and GI disturbances such as nausea, abdominal pain, vomiting, anorexia, hepatic and renal damage and hypertension (WHO 2000b). Few haematological effects have been experienced after an acute exposure to Pb (ATSDR 1999c), and Pb concentrations of 48 - 120 µg/dL have caused hypertension (WHO 2000b). In addition to that the acute exposure of Pb may cause an acute nephropathy and the effects on renal function have been reported at PbB concentrations of 40 µg/dL (WHO 2000b). While the chronic effects are nephropathy and renal tubules dysfunction (RAIS 1994). Although chronic exposure may cause chronic nephropathy at Pb concentrations of 50 - 200 µg/dL (WHO 2000a). As well as the chronic Pb exposure may cause adverse effects on the reproductive functions of male and female (ATSDR 1999c), in male a decreased of sperm motility, reduced libido, sperm counts and low semen volume, can occur (WHO 2000b, IPCS 1995). Neurological effects may be noticed such as sleep disturbance, headache, fatigue, irritability, convulsions, lethargy, slurred speech, muscle tremors, weakness and paralysis (IPCS 1995, ATSDR 1999c). Epidemiology studies assumed that there are no completely harmless levels of Pb exposure. These studies have reported that the inverse relationship between IQ (Intelligence Quotient) and blood Pb concentrations is above 10 µg/dL by children. Other chronic Pb effects are anemia and decreased hemoglobin synthesis (IPCS 1995, ATSDR 1999c). Although reduced post-natal and low birth weight have been observed with PbB concentrations of 10.4 µg/dL (NPIS 2003). Children who are exposed to Pb during foetal or during the first years of their life may have encephalopathic symptoms, lower IQ, nerve damage, delay growth, behavioural problems and death may occur

with Pb concentrations 80 - 100 µg/L (RAIS 1994). Only in few cases there was hepatic damage after occupational exposure to Pb (ATSDR 1999c), also increase in sister chromatid exchange and chromosomal aberration has been caused by occupational exposure to Pb (IPCS 1995). Workers have also suffered from gastrointestinal disturbance such as vomiting, constipation, anorexia, nausea, and abdominal cramps with Pb concentrations of 100 - 400 µg/dL following the chronic Pb exposure (WHO 2000b, ATSDR 2005d). Female workers who have been exposed to Pb in occupational places before or during pregnancy may experience low birth weight, stillbirths or spontaneous abortion (RAIS 1994). The Committee on Toxicity (COT) of Chemicals in Food Consumer Products and the Environment reported the impossibility to establish a threshold of Pb effect (COT 2003). Finally the International Agency for Research on Cancer (IARC) reported that inorganic Pb compounds are probably carcinogenic to humans (DEFRA and EA 2002).

## 2.8 Uranium

Uranium (U) is a heavy, radioactive, silvery white, weakly element with atomic number 92. It and all of its decay products are heavy metals except radon gas; the natural U has a low level of radioactivity because of its long life, it is 4.5 million years (Weir 2004). U is a very active metal; it reacts with air and forms oxides. It can also react with most elements except rare gases. U occurs naturally in four valences, which are the predominant species in the environment, and they explain the potential toxicity of U (Schnug et al. 2002). Natural U consists of mixture of three radioactive isotopes, U-238, U-235 and U-234, they are similar in their chemical properties, and in their chemical effect on human body, but they are different radioactive materials with different radioactive properties (ATSDR 1999a). U occurs naturally in various mineral deposits especially in granite rocks. It is widely distributed in nature and it presents commonly in the environment, in soil, seas, rocks, water, plants, animals and humans in various chemical forms (Schnug et al. 2002). U concentration in the earth's crust is about 2.7 mg/kg (Bernhard 2005), and exists in soils in low varying concentrations ranged between 0.1 and 11 mg/kg (Schnug et al. 2002). U concentrations in air are also very low and ranged between 0.02 ng/m³ - 0.1 ng/m³ with selected value 0.076 ng/m³ (Bernhard 2005).

Human and animals can be contaminated by U in different ways: inhalation, ingestion and contact. The inhalation is not so important as food and water, and the contact is important for the people that work directly with U, and in the actually days for the people that live in those places where the war is part of life. The ingestion of U can be through the drinking water and

food chain, by animals that are contaminated and plants that are able to up take the soluble form of U. More than 95 % of ingested U from food or water is not absorbed and leave the person's body within few days in the faeces, and absorbed U ranged between 0.1 % and 6 % of the oral dose (EFSA 2009). A small amount of this absorbed U will go into blood and then it will excrete in the urine during few days. The rest remains in kidneys, or other soft tissues, and bones where it will stay for years (ATSDR 1999b). Mammals have a particular high sensibility to U (Fellows et al. 1998). Once the U is in the organism, it is transferred to the extracellular fluids and transported through the blood to others organs, uranyl ($UO_2^{2+}$) is the soluble form transported and it forms complexes with protein and anions. The U that is not retained is eliminated by the urinary and faecal excretion the retained in the organism has two parts: the biological is linked with mechanisms and kinetic of U transfer for the other organs, and the physical that is linked with the emission of radioactivity. The risks related with the exposure to U can be chemical and radiological. The first one is related with the binding of U to biological molecules. This risk is particular high for kidneys because of peak concentrations during the excretion process. The second one is the radiation which is of particular risk for lungs and bones. The liver and spleen are prominent places of U accumulation. The most remarkable effect of U toxicity going along with low and medium contaminations is cancer. Thus increasing rates of kidney failure in humans over the last twenty years have been already suspected to contribute at least partially to the chronic increase of mineral water consumption, which causes a considerably higher U uptake (Schnug et al. 2005). Schnug and Lindemann (2006) found that between 1986 and 2004 with a certainty of 97 % both the mineral water consumption, and the frequency of kidney replacement therapy in Austria, Germany and the USA increased by the same extent (approximately 5 % per year). Compared to this mutation is a phenomenon only associated with very high U contamination of organisms. The dangers arising from the biochemical toxicity of U are generally considered to predominate the risks from its radioactivity (Milvy and Cothern 1990). Historically, U has been considered both a radiological and also a 'heavy metal' poison, following calcium in its distribution within the body, i.e. building up in bone, and with the principle target for toxicity being the lung and the kidney (Royal Society 2001). More recently, it has been shown that U also targets the brain (ENVIRHOM 2006). The dangers arising from the biochemical toxicity of U are generally considered to overweigh the risks from its radioactivity (Milvy and Cothern, 1990). As a basis to assess the chemical toxicity of U, occupational limits of a selection of heavy metals and other toxic substances are listed in table 1 presented by Busby and Schnug (2008) the heavy metals listed, apart from U

(!), are those, which are regulated, in the "German ordinance for soil protection" (BBodSchV). It is worth mentioning here that U concentrations in soils are not covered by any legal regulation in the great majority of countries in the world.

The chemical toxicity of U is ranked between that of Hg and Ni if based on MAC values (tab. 1, chapter 1). Gamma rays are reported to severely damage DNA in the presence of U, which indicates a synergistic effect between both hazards. The photoelectric effect has been identified to cause this combination effect: U bound to phosphate groups of DNA absorbs gamma rays from the proximity, which results in the release of secondary electrons (beta rays) in addition to the original alpha radiation so that the overall radiotoxicity of U increases (Busby and Schnug 2008). The ENVIRHOM studies (Henner 2008) reveal that a U concentration of >10 µg/L induces reactions to oxidative stress in aquatic organisms and genotoxicity may occur. Latest research reports also an estrogenic effect of U. Noteworthy in this context is the fact that the toxicity of U can be multiplied synergistically by Cd. Hereby, the distinctly stronger radiological and chemical toxicity of U decay products (particularly Po, Ra and Rn) has not been considered. There is general agreement among scientists that irrespective of relations and interactions of detrimental effects the radioactivity of U on its own does not permit to educe critical values. Rather the ALARA principle (As Low As Reasonable Achievable) should be the basis for decisions on abatement measures. Consumers reserve the right to be protected from hazardous compounds in foods and drinks. U is such a hazardous compound with the feature that U is in all foods and all drinks in certain amounts and that U has two modes of damaging, by its radioactivity and by its chemical toxicity. The question arises as to which amounts can be safely tolerated and under what circumstances. From scientific point of view, and especially in the case of U, hazards depend very much on the circumstantial parameters assumed and never consider interactions between individual susceptibilities (e.g. diseases, low immunity, genetic conditions) or other hazardous substances and influences on the organism in question. Doses and risks from internal radiation are still burdened with many uncertainties (Fairlie 2005). Obviously considering Gofman´s (1996) statement that there is no safe dose for radioactivity, U.S. EPA has set a goal of no U in drinking water (ATSDR 1999b) and calls this the "Maximum Contaminant Level Goal (MCLG)", but recognises that currently there is no practical way to meet this goal. Because of this, U.S. EPA proposed in 1991 to allow up to 20 µg of U per litre (20 µg $L^{-1}$) in drinking water, and states began to develop regulations to achieve this level. U.S. EPA calls this the Maximum Contaminant Level (MCL). The MCL for U is based on the calculation that if 150,000 people drink water that contains 20 µg $l^{-1}$ of U for a lifetime, there is a chance that

one of them may develop cancer from the U in the drinking water. Important to mention here that low probabilities are subliminally connected to large time scales. But it is part of nature that there is, admittedly a faint chance, that just one U atom spontaneously causes cancer in an organism and in this case the risk is always 100 % for the victim of circumstances. Worried about possible hazards the BfR claimed already “U free” waters for nurslings (BfR 2005). Apart from the fact that the U concentration of water can only be lower than the technical detection limit of contemporary state of the art analytical techniques and never zero, the claim also does not specify the target group in question: according to ICH guidelines there are “newborn infants (0 to 27 days old) and infants and toddlers (28 days to 23 months old)” (ICH 2000). Shortly after BfR defined “free of U” as concentrations < 0.2 µg/L U, which is 13 times more than the technically LLD. The discussion becomes preposterous with the release of a guideline value of 10 µg/L U by the same authors who pleaded just 5 years earlier, and still based on the unchanged facts supplied by the WHO (1996 & 2004), for 1 µg/L U (Dieter 2000, Konietzka et al. 2005). Most recently the WHO changed her mind again and proposes now a value of 30 µg/L U as lifelong acceptable concentration (Anonymous 2011). Their main reasoning for this is the "impracticability" of the lower values for today's drinking water supplies, which can be interpreted as a clear indication for an increasing U contamination through non point (diffuse) pollution of drinking water bodies coming from anthropogenic sources.

## 2.9 Zinc

Zinc is a lustrous bluish-white metal which spreads naturally in the air, soil and water, and it is found in all foods (Thomas 1991, ATSDR 2005c). It is one of the most abundant elements in the earth’s crust with concentration of about 70 mg/kg (Thomas 1991, ATSDR 2005c). Its concentration in the air of urban areas is ranged between 100 and 500 ng/m³, while it is between 10 - 100 ng/m³ in rural areas (WHO 1996). Natural processes release part of Zn into the environment, while most of it in the environment comes from human activities including mining activities, metal smelters like Zn, Cd and Pb, die casting metal, rubbers, steel and alloys production, waste and coal burning, and use of Zn fertilisers in agriculture (ATSDR 2005b). Zn is used mainly in galvanized metals and metal alloys, where Zn is mixed with other metals to form alloys such as bronze and brass, and pennies in United State are made of Zn-Cu alloy (ATSDR 2005b). Zn combines with other elements such as sulfur, chlorine, and oxygen to form Zn compounds such as Zn sulfate, Zn sulfide, Zn chloride and Zn oxide,

which are widely used in industry (ATSDR 2005b). Zn compounds have also commercial applications as chemical intermediates, UV-stabilisers, rayon manufacture, soldering fluxes, mildew inhibitors, antiseptics, deodorants, astringents and mordant for printing and dyeing. Zn salts have several applications such as wood preservation, photographic paper, catalysts, ceramics, fertilisers, batteries, pigments, textiles, in vulcanisation acceleration for rubber and as medicines or nutritional supplements (ATSDR 1989, ATSDR 1995). Zn chloride, Zn oxide, Zn sulfate, and Zn sulfide are used in medical, dental, and household applications as well as Zn chloride and Zn sulfate are also used in herbicides. Finally Zn chloride is a main component of smoke bombs (ATSDR 1995). It has been noticed that the concentrations of Zn in tap water can be higher from its concentrations in surface and ground waters this is due to Zn leaching from piping and fittings (WHO 1996). Whereas its concentration in groundwater is generally between 10 - 40 µg/L, and less than 10 µg/L (WHO 1996). The recommended concentration by U.S. EPA in drinking water should not exceed 5 mg/L. Zn is an essential element for human nutrition. It is the most abundant element in the human body, and it is essential for the function of more than 300 enzymes (Stefanidou et al. 2006). The major human dietary sources of Zn are dairy products, meats, grains, and mixed dishes (Pennington et al. 1989). The daily requirement of Zn is between 15 - 22 mg/day for adults (WHO 1996), and the recommended daily allowances of Zn are 15 mg, 12 mg, and 15 mg for adult male, adult female and pregnant woman respectively (NRC 1989), and it is 5 mg for infant 0-12 months old, and 10 mg for children older than one year (NRC 1989). The contribution of drinking water in the total daily Zn intake man of human is negligible and in some cases depends on the leaching of Zn from corrosion of piping and fittings (WHO 1996). The gastrointestinal absorption of Zn is 20 - 30% in individuals with normal levels of Zn in their bodies (RAIS 1992). It is mainly absorbed in the small intestine with variable percentages from 20 % to 80 %. In addition the amount of Zn in the body, its chemical status, and the dietary levels of other nutrients or other trace elements like Cu, Pb and Fe can influence Zn absorption (U.S. EPA 1984), as an example Zn absorption may be reduced with excessive levels of both Cu and Sn in the diet (Valberg et al. 1984). Zn is present in all tissues, but high concentrations exist in the heart, pancreas, liver and kidney (RAIS 1992), and its highest concentrations are in prostate gland (Bertholf 1988). The average of Zn excretion from the body depends on both past Zn content in the body and current Zn intake. It is primarily excreted via the gastrointestinal tract in the faeces, with small amounts in the urine, sweat and semen (RAIS 1992). Approximately 14 % of the eliminated Zn excretes in urine in normal Zn intake, but it increases to 25 % when Zn dietary intake increases (Wastney et al. 1986). As

mentioned before, for a good health, Zn is an essential element in low levels for all living being, including humans and too little Zn in the diet may be cause adverse health effects, while too much Zn is harmful (ATSDR 2005c). In humans, Zn deficiency has general symptoms such as hypogonadism, night blindness, mental lethargy, retarded growth, anorexia, loss of appetite, decreased sense of taste and smell, slow wound healing, and skin changes (Prasad 1983). It can also impair the immune system (Baer et al. 1985). Exposure to large diet amounts of Zn, which equal to 0 - 15 times higher than the adequate levels of Zn in humans may be harmful and adverse effects can be observed (ATSDR 2005c). A common symptom of acute oral exposure to Zn compounds is gastrointestinal distress (ATSDR 1989), and the other reported symptoms include abdominal cramps, nausea, vomiting, diarrhoea, headache, and lethargy. In addition, gastrointestinal bleeding and haematological signs of anaemia may occur at high doses of Zn (RAIS 1992). Toxic health effects have been reported to the respiratory system from inhalation of high concentrations of some Zn compounds (ATSDR 1989). Inhalation of Zn oxide fumes can cause "metal fume fever" (Bertholf 1988) and its main symptoms are cough, headache, fever, weakness, sweating, hyperpnoea, nasal passage irritation, lung volume reduction, altered taste, and pains in the legs and chest (RAIS 1992). More severe effects from Zn inhalation can result such as dyspepsia, cough, headache, fever, nausea and vomiting, chest pain, nose and throat irritation, acute pneumonitis, and pneumothorax (ATSDR 1989). The occupational exposure of Zn compounds may cause gastrointestinal symptoms to the workers including nausea, vomiting, anorexia, weight loss, epigastric discomfort, respiratory distress, hypocalcaemia, and leukocytosis (U.S. EPA 1991a), and The Occupational Safety and Health Administration (OSHA) has estimated the average of Zn chloride fumes and Zn oxide in workplace air during 8-hour workday or 40-hour workweek were 1 mg/m³ and 5 mg/m³ respectively (ATSDR 2005b). Due to insufficient evidences of Zn carcinogenicity in human and animals, the U.S EPA (U.S. EPA 1991a), the International Agency for Research on Cancer (IARC) and the Department of Health and Human Services (DHHS) have not classified Zn as carcinogenic element in humans (ATSDR 2005c).

# 3 Material and Methods

## 3.1 Origin of mineral and tap water samples

***Bottled waters*** derived from a worldwide survey conducted by the former Institute of Plant Nutrition and Soil Science of the Federal Agricultural Research Centre in Braunschweig, since 2008 till recently the Institute for Crop and Soil Science of the Julius Kühn Institute in Braunschweig, Germany (PB) including 1154 different brands of which 363 are of true German origin, with data on U and other chemical elements. U concentrations and concentrations of other elements in those waters have been analysed by PB or collected from published sources. In addition to the samples analysed at FAL the database contains also element concentrations for brands reported in scientific literature. Data sets retrieved from literature have been validated through U analyses at FAL (Knolle 2008).

The samples analysed by PB were purchased between 2000 to 2007 from regular stores. Individual data for each brand and each analytical parameter are available in Knolle (2008) and www.strahlentelex.de. The last update of the mineral water database used for this study was on July 24, 2009 with data provided by Oekotest (2009). The database is continuously updated, latest with data derived from Reimann and Birke (2010).

The author would have been glad to add the 1456 mineral water data sets the BfR (2005) was strutting around to this data base. However, there are only 807 accredited mineral waters on the official German list (BVL 2008) which means that this number is bogus any way and, if this data set really exists and because its more or less unlikely that it covers the entire number of 807 origins it must contain quite a number of repeated measurements of individual waters which makes even the aggregated statistical data published out of it (BfR 2005; EFSA 2009, c) quite questionable. Also the Federal Office for Radiation Protection (BfS) published data on the radioactivity of 366 specified mineral waters of German plus 35 from European countries (BfS 2006) but even on an official request for cooperation between two federal research organisations BfS denied access to information of the equivalent doses of individual nuclides in the waters.

In the dietary scenarios the mineral water samples were grouped according to the country of origin: “world mineral waters” comprises the entire 1456 brands, “German mineral waters” the 366 brands which source is located in Germany and “German and neighbouring countries”

those which source is located in direct neighbour countries of Germany (Austria, Belgium, Czech Republic, Denmark, France, Hungary, Poland, Switzerland and the UK) and German mineral waters.

***Tap waters*** are usually sampled according to DIN (2004) but for the FAL campaign, where the samples were not taken by professional sampling personnel a simple and easy but highly reliable method was developed.

With view to maximum efficiency of the survey (fast, low cost, reliable) the samples were collected by individuals who responded to a chain letter action launched by FAL-PB in August 2006. A preliminary selection aimed primarily at collecting samples from German communities with more than 50.000 inhabitants. 266 individuals (97 % of the entire group involved) delivered 471 samples representing gecoded 458 locations.

In order to minimise the sampling error the participants were asked to employ a simple, but standardised sampling procedure. As sampling containers freshly emptied 500 ml polyethylene Diet Coke® bottles were stipulated, because their inward walls had been continuously been in contact with an acidic, heavy metal free buffer solution (Schnug et al., 1996) and thus any adsorbing properties were supposed to be saturated with protons and which also contained no sugars of which traces may have promoted the growth of micro organism during time elapsed until the samples arrived at the laboratory. The suitability of the sampling method has been checked in the laboratory through the recovery of U from aqueous U standard solutions found to be within the combined averaged repeatability of the methods used for U analysis (ICP-QMS and alpha spectroscopy) which amounts to ± 13.3 % deviation of means (calculated from 95 % confidence interval for the regression of 208 sample pairs from 17 different sources, $r^2$ = 89.6 % (Knolle 2008). The entire data set has been enlarged with 299 data sets from Schäf et al. (2007). In addition for U were 2911 data sets collected from official county services by foodwatch in 2009, 65 from the so called "German Environmental Survey on Children" (Schulz et al., 2008) and 168 from the BfS survey (Beyermann et al., 2009). For U in total 4092 non redundant data sets were available, for the elements As, Cu, Ni and Pb 750 ones and for the elements B, Li, Mo and Zn 458 ones. Of the 4092 data sets for U 9.5 % originated from the FAL survey (Knolle 2008), 7.2 % from Schäf et al. (2007), 1.7 % from Schulz et al. (2008), 77.5 % from foodwatch (2009) and 4.3 % from the BfS (Beyermann et al. 2009) survey.

The distribution of the samples for U within Germany is shown in fig. 1.

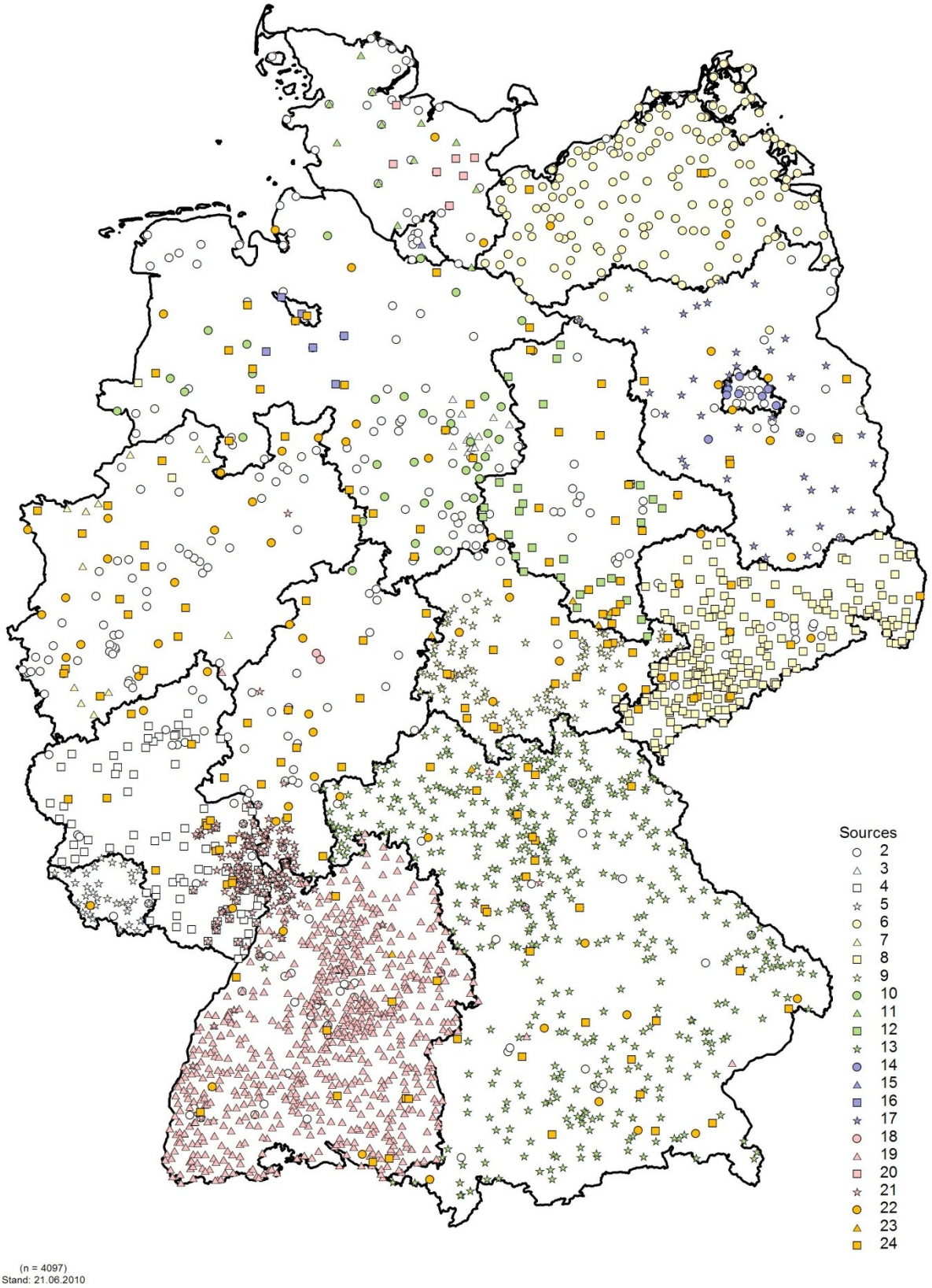


Figure 1: Locations of tap water samples in Germany (n = 4092)
Sources: 2-3 FAL/JKI, 4-20 Country Reports, 21 Schäf, 22 UBA, 23 foodwatch, 24 BfS

***Geocoding of samples***

A geological evaluation of the origin of U in the German mineral waters is given by Knolle (2008). In order to assess the population with potential access to a particularly quality of tap water the tap-water data were geocoded by means of the 5 digit German postcode. The actual population number for each post code was retrieved from the most recent entry to the internet. However the German postcode system has cases where the same town name has more than one postcode (e.g. Aachen: 52064, 52068, 52070) or the same postcode is attributed to more than one town (e.g. postcode 01651 stands for: Lampertswald, Schönfeld, Tauscha, Thiendorf, Weissig). In the case where the same town name has more than one postcode and if for the subunits of the postcode no individual population numbers were available, the total population number for the town found in the internet (in this example for Aachen = 258,772) was divided by the number of data sets for the town (in this example 4).

In the case where the same postcode was attributed to more than one town the most recent population number for the particular town was taken from the internet.

If for the same postcode and the same town name more than one U measurement was available (e.g. 2 entries for post code 01665 “Käbschütztal”) and if the difference from the combined mean (value A: 0.15 µg/L U / value B: 6.20 µg/L U: combined mean = 3.23 µg/L U) was smaller than the 95 % confidence interval given for this mean in tabs. 4&5 (10 % = ± 0.32 µg/L U) they were made separate entries to the data. Otherwise the values were averaged and made to one single entry on either the same postcode or the same town name.

Information about the population coverage for the different elements in German tap water are given in tab.3.

Table 3: Number of available data sets for As, B, Cu, Li, Ni, Mo, Pb, U and Zn in German tap water and size of the population with potential access to these waters

| **Elements** | **N of data sets available** | **Population covered** | **% of total German population** |
|---|---|---|---|
| **U** | 4092 | 60,354,408 | 73.4 |
| **As, Cu, Ni, Pb** | 750 | 29,551,132 | 35.9 |
| **B, Li, Mo, Zn** | 458 | 27,242,389 | 33.1 |

## 3.2 Chemical analysis

***Element concentrations***

After pressure digestion with nitric acid the isotopes (natural abundance (%) in brackets) $^{75}As$ (100), $^{11}B$ (80), $^{63}Cu$ (69.17), $^{7}Li$ (93.5), $^{98}Mo$ (24.13), $^{58}Ni$ (68.27), $^{208}Pb$ (54.4), $^{238}U$ (99.275) and $^{64}Zn$ (48.6) were analysed directly by means of inductively coupled quadrupole plasma mass spectrometry (ICP-QMS, Taylor, 2001) employing a VG-Elemental Plasmaquad 4 instrument. The total element concentrations where calculated through the ICP-QMS is an analytical technique where an (usually) aqueous sample is nebulised to an aerosol which is transported into a plasma by an argon gas stream. "Inductive coupling" is the process which sustain the plasma by a cascading collision of electrons accelerated in the outer spheres of the plasma by radio frequency (typically 700-500 W, ~ 27 MHz frequency) with argon atoms. In the plasma at temperatures between 7.000 - 11.000 K the elements in the sample are atomized followed by immediately ionisation. Ions are representatively sampled from the plasma into the high vacuum of a quadrupole spectrometer. Quadrupoles are electromagnetic mass filters through which only ions of a pre-selected mass can pass onto a detector, where they are converted into a measurable electric current (Taylor 2001).

The most important feature of ICP-QMS is that unlike with radiochemical (DeCamargo and Mazilli 1996) or optical emission spectroscopy from an ICP source (ICP-OES) (Dadfarina and McLeod 1994; Miura et al. 2000) no enrichment steps are required for the concentration range in question.

The theoretical lower limit of detection (LLD) for $^{238}U$ by ICP-QMS is 2 ng $l^{-1}$ (El-Himri et al. 2000), but practically the LLD was found to be 15 ng $l^{-1}$, which fits well with the 13 ng $l^{-1}$ reported by UNEP (2001). The practical detection limits for the other elements were: 0.33 µg/L for As, B, Cu, Ni and Zn, 0.16 µg/L for Li and 0.03 µg/L for Mo, Pb. The concentration for samples with readings lower than the LLD were set to ½ of the LLD respectively.

***TDS (Total Dissolved Matter)*** according to manufacturer's information on bottle labels or publications. Where not available, TDS was evaluated through a regression established from the samples with known TDS and the concentration of the major mineral constituents. TDS correlated with the elements investigated in this study as follows:

As 0.209**, B 0.192**, Cu 0.061 n.s., Li 0.333**, Mo 0.239**, Ni 0.224**, Pb –0.016 n.s., U 0.766**, Zn 0.127*.

The frequency analysis of the TDS in 2134 mineral waters of the database suggested a division of the data into three classes according to their TDS (fig. 2):

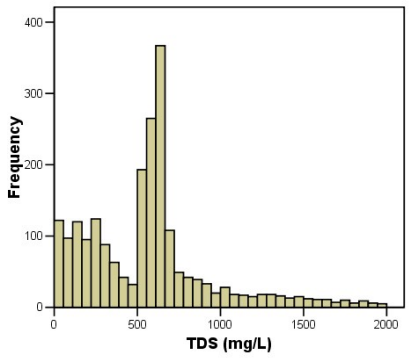


Figure 2: Frequency of total dissolved matter (mg/L) in 2134 mineral waters (world mineral water database)

Examples of well known brand names for the three classes are: low mineralised waters: SPA Barisart (49), Volvic (109), Wittenseer Quelle (425); medium mineralised waters: Ramloese (817), Vittel Bonne Source (841), high mineralised waters: Apolinaris (2767), Heppinger (4566), Westerwald-Quelle (8500).

***Quality control of analytical data***

The main quality control measure at the laboratory of FAL-PB, additionally to the adoption of principal rules of GLP (BfR 2009) is the continuous participation in WEPAL, i.e. Wageningen Evaluation Programmes for Analytical Laboratories (Dijk and Houba 1998).

Due to the fact that the databases originate from different sources a number of entries were overlapping, meaning, that a particular mineral water was collected twice or more at different times and locations and analysed by different laboratories, or in a particular postcode region or town tap water was collected twice or more at different times and locations and analysed by different laboratories. In the mineral water and tap water databases the results of such overlapping data were averaged or treated as a population subgroup of a region (see above), but also collected in an own data base for the assessment of the quality of sampling and analysis. The results of regression analysis in overlapping data for the elements As, Cu, Ni,

Pb, and U are presented in tab. 4, fig. 3 shows the result graphically for the 639 data pairs for U.

Table 4: Linear regression (y = b*x + c) between data of repeated measurements of As, Cu, Ni, Pb in tap waters and U in tap and mineral waters (same postcode, different sample, different laboratory)

| | **As** | **Cu** | **Ni** | **Pb** | **$U_{(n = 71)}$ *** | **$U_{(n = 639)}$ **** |
|---|---|---|---|---|---|---|
| **Mean FAL-PB (y)** (µg/L U) | 1.39 | 93.8 | 1.32 | 0.88 | 0.76 | 1.02 |
| **Mean External-lab (x)** (µg/L U) | 1.86 | 51.1 | 1.05 | 0.81 | 0.85 | 1.06 |
| **N** | 35 | 21 | 21 | 21 | 71 | 639 |
| **$r^2$ (%)** | 61.9 | n.s. | 24.8 | 10.3 | 80.0 | 94.6 |
| **B** | 0.322 | -- | 0.538 | 0.186 | 0.911 | 0.969 |
| **Constant** | 0.793 | -- | 0.799 | 0.733 | -0.013 | -0.007 |
| **CI for X = 1 (± % of mean)** | 40 | -- | 83 | 73 | 29 | 6.2 |
| **CI for X = 10 (± % of mean)** | 31 | -- | 83 | 54 | 14 | 3.7 |
| **CI for X = 20 (± % of mean)** | 29 | -- | -- | -- | -- | 3.2 |

Remarks:
* FAL lab vs. Schäf et al. (2007): ** FAL lab vs. 24 different sources (see also Knolle, 2008, CI: 95 %-confidence interval).

The values given in tab.3 for the 95 %-confidence interval would indicate the reproducibility of the procedure, which according to prevalent definitions “is the variability of the measurement system caused by differences in operator behaviour” (ES 1999). Those values are excellent low for U, suggesting a high stability of the U concentrations even under variable sampling and laboratory conditions (fig. 3). For Cu no significant regression could be established, suggesting that the Cu concentrations are very much influenced by highly variable contaminations deriving from differences between the plumbings of the sampling location. In contrast to this Schulz et al. (2009) report quite a small 95 %-confidence interval for their measurements of Cu in tap waters (tab.5). This value, however, is biased because the given number of 1029 samples were taken on only 150 locations indicating a more than 6 fold replication of each sample. Thus the 95 %-confidence intervals reported by Schulz et al. (2009) indicate more the repeatability of the procedure, which according to prevalent definitions is the variability of the measurements obtained by one person while measuring the same item repeatedly. This is also known as the inherent precision of the measurement equipment” (ES 1999).

Table 5: Comparison of descriptive statistics for Cu, Ni, Pb and U concentrations (µg/L)in German tap waters reported by EFSA, FAL-PB and UBA and U in mineral waters reported by EFSA and FAL-PB

| Element | Source | N | P5/P10 | Mean | Median | P95 | Maximum | CI-Median[e] |
|---|---|---|---|---|---|---|---|---|
| **Cu in tap Water** | FAL-PB | 750 | 1.74/3.52 | 78.8 | 19.5 | 356 | 2826 | F |
| | UBA[a] | 150 | -.--/9.10 | 197 | 69.9 | 805 | 5280 | 63.4-77.2 |
| | | | | | | | | |
| **Ni in tap Water** | FAL-PB | 750 | 0.21/0.21 | 3.74 | 0.882 | 5.56 | 607 | 0.09-1.90 |
| | UBA[a] | 150 | -.--/1.00 | 3.70 | 3.48 | 9.00 | 89.7 | 3.36-3.60 |
| | | | | | | | | |
| **Pb in tap Water** | FAL-PB | 750 | 0.00/0.00 | 1.07 | 0.310 | 3.06 | 199 | 0.13-1.27 |
| | UBA[a] | 150 | -.--/0.20 | 1.53 | 0.610 | 4.90 | 83.4 | 0.56-0.66 |
| | | | | | | | | |
| **U in tap Water** | PB-FAL[b] | 4092 | 0.03/0.10 | 1.67 | 0.500 | 7.21 | 49.0 | 0.43-0.53 |
| | UBA[a] | 150 | -.-/<0.001 | 0.66 | 0.169 | 3.16 | 19.4 | 0.15-0.19 |
| | EFSA[c] | 97 | 0.05/-.-- | 0.43 | 0.500 | 1.80 | 10.5 | n.a. |
| | EFSA[cc] | 4833 | 0.03/-.-- | 3.09 | 0.725 | 9.27 | 93.0 | n.a. |
| **U in bottled water** | FAL-PB[d] | 1154 | 0.00/0.00 | 3.45 | 0.300 | 8.43 | 474 | 0.21-0.32 |
| | FAL-PB[dd] | 775 | 0.00/0.00 | 3.92 | 0.300 | 10.0 | 474 | 0.21-0.32 |
| | FAL-PB[ddd] | 362 | 0.00/0.00 | 1.45 | 0.161 | 8.48 | 27.4 | 0.08-0.18 |
| | EFSA[c] | 1224 | 0.02/-.-- | 1.19 | 0.325 | 5.30 | 10.5 | n.a. |
| | EFSA[cc] | 2207 | 0.03/-.-- | 3.18 | 0.440 | 8.40 | 153 | n.a. |

Remarks:
[a] random sample, mean of 1029 measurements from 150 locations (Schulz et al. 2009)
[b] FAL-PB entire German tap water data base
[c] EFSA (2009) Germany only (see comments in text above!) [cc] EFSA (2009) entire database for EU
[d] FAL-PB world mineral waters; [dd] FAL-PB German and neighbouring EU countries; [ddd] FAL-PB
[e] 95 %-confidence interval for median
f no significant correlation between independent sampled and analysed samples

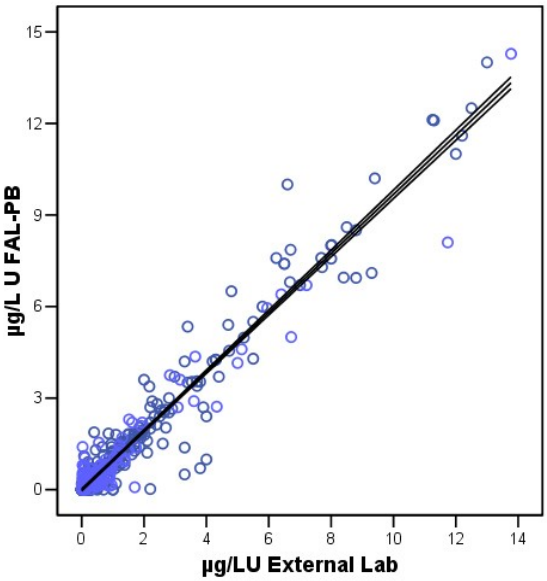


Figure 3: Scattergram of U concentration in 639 samples analysed by different laboratories ($y = 0.969\ x - 0.007$, $R^2 = 94.6\ \%$)

### 3.3 Dietary scenarios

The main objective of this study was to evaluate the relative significance of water to the total daily intake of the elements As, B, Cu, Li, Mo, Ni, Pb, U and Zn. This evaluation requires information about the amount of intake deriving from solid foods. EFSA (2009) provides a so called "Concise European Food Consumption Database" which holds food consumption data reported from the individual EU countries. EFSA (2009) itself mentions the different methodologies employed for data collection as the main limitation of the database. This results in sometimes very different consumption pattern between different countries. According to the data stored for instance a Dane would consume nearly 6 times as much liquid than a Bulgarian citizen. Another limitation highlighted by EFSA (2009) is the "broad food categories used". However, in this study an assembling of the considerably variable food sources human diet in only a few broader categories was adopted as a mean to achieve a low bias from element intakes through solid foods.

Therefore, in this study a standardised healthy diet has been designed based on an energy requirement of 2000 kcal/day (Eastwood 2003) and the rules of the well known "nutrition pyramid" (fig. 4, Anonymous 2010)


Figure 4: The food pyramid

(From http://web.mit.edu/athletics/sportsmedicine/Food Pyramid.JPG)

For this standard diet it was adopted that 55 % of the total energy demand derive from carbohydrates, 15 % from protein (5 % milk and milk products, 10 % meat/fish/shellfish and meat/fish/shellfish products) and 30 % from fats (15 % from milk and milk products, 15 % meat/fish/shellfish and meat/fish/shellfish products).
This is more or less equivalent to a daily diet of 314 g cereals and cereal products, 122 g meat/fish/shellfish and products of them ((meat/fish = 6:1) includes 2 % offal), 120 g milk/egg and products of them, 320 g vegetables and fruits (of which 44 % leaf vegetables 38 % root vegetables and 18 % fruits).

The assumed average energy content of the food categories above were: cereal and cereal products: 350 kcal/100 g, fish/shellfish and fish/shellfish and products of them (10 % fat): 100 kcal/100 g, meat and meat products including offal and products of them (20 % fat): 250 kcal/100 g (at a ratio of meat/fish = 6 : 1 the average energy content of this source would be 228 kcal/100 g), milk, eggs and products of them (20 % fat): 250 kcal/100 g, vegetables and fruits: 60 kcal/100 g.

The standard diet has been diversified in three additional diet types: an ovo-lacto vegetarian, a vegan and a carnivore type. The percentage of energy input from the different food categories defined above to the total of 2000 kcal/day is shown in tab.6 and in addition the average mass consumption of different food categories to maintain an energy input of 2000 kcal/day in tab.7.

Table 6: Relative contribution of different food categories to the energy input (2000 kcal/day) in different diet types

| **Diet type** | **% Energy input from food category** | | | |
|---|---|---|---|---|
| | Cereals and cereal products | Meat/fish/shellfish and products of them | Milk/egg and products of them | Vegetables and fruits |
| **Standard** | 55 | 14 | 15 | 16 |
| **Vegetarian (ovo-lacto)** | 50 | -- | 25 | 25 |
| **Vegan** | 60 | -- | -- | 40 |
| **Carnivore** | 30 | 50 | 10 | 10 |

Table 7: Average consumption (g/day) of different food categories to maintain an energy input of 2000 kcal/day with different diet types

| **Diet type** | **Daily consumption (g/day) from food category** | | | |
|---|---|---|---|---|
| | Cereals and cereal products | Meat/fish/shellfish and products of them | Milk/egg and products of them | Vegetables and fruits |
| **Standard** | 314 | 123 | 120 | 355 |
| **Vegetarian (ovo-lacto)** | 286 | -- | 200 | 833 |
| **Vegan** | 343 | -- | -- | 1333 |
| **Carnivore** | 171 | 439 | 80 | 333 |

### 3.4 Meta-data of element occurrence in solid foods

Meta data for concentration for As, B, Cu, Li, Mo, Ni, Pb, U and Zn for the different food categories mentioned above (chapter 3.3) were collected through a selective literature research. In statistic a meta-analysis combines the results of several studies that address a set of related research hypotheses. The results of the meta-analysis for the food categories are collected in tab.8.

Table 8: Mean occurrence concentrations (mg/kg) of As, B, Cu, Li, Mo, Ni, Pb, U and Zn in the food categories “cereal and cereal products”, “meat/fish and products of them”, “milk/eggs and products of them” and “vegetables/fruits and products of them”. (Individual data and full descriptive statistics are collected in annex, tables 37 - 45)

| Element | Cereals and cereal products | Meat / fish and products of them | Milk / eggs and products of them | Vegetables / fruits and products of them |
|---|---|---|---|---|
| **As** | 0.09 | 3.32 | 0.01 | 0.03 |
| **B** | 3.5 | 0.63 | 0.43 | 5.06 |
| **Cu** | 1.92 | 11.3 | 0.69 | 1.95 |
| **Li** | 0.21 | 0.07 | 0.07 | 0.1 |
| **Mo** | 0.41 | 0.38 | 0.14 | 0.46 |
| **Ni** | 0.38 | 0.18 | 0.05 | 0.37 |
| **Pb** | 0.07 | 0.11 | 0.03 | 0.15 |
| **U** | 0.002 | 0.002 | 0.001 | 0.001 |
| **Zn** | 15.5 | 25.7 | 10.5 | 5.67 |

According to the results gathered in tab.9 the highest mean concentrations for As, Cu, U and Zn are found in food from the category “meat/fish and products of them”, for Li and NI in the category “cereals and products of them” and for B, Mo and Pb in the category “vegetables/fruits and products of them”. The lowest mean concentrations (except for Zn) for all elements covered by the research work here occur in the category “milk/eggs and products of them”, for Zn the lowest mean concentration occur in food from the category “vegetables/fruits and products of them”.

### 3.5 Analytical data of element occurrence in mineral and tap waters

The basic descriptive statistics for the mineral and tap waters used in this study are already published in Knolle (2008), Knolle et al. (2011) and Smidt et al. (2011). The tables below summarise only the mean and P 95 occurrence data which, according to EFSA procedures, are used in the research work presented here.

Table 9: Mean and P 95 concentration of As, B, Cu, Li, Ni, Mo, Pb, U and Zn concentration in mineral waters (from the world, from Germany and neighbouring countries, from Germany) and German tap water (µg/L). Individual data and full descriptive statistics are collected in Knolle (2008)

| | Mineral Water | | | | | | German tap water | |
|---|---|---|---|---|---|---|---|---|
| | World | | Germany and neighbouring countries | | Germany | | | |
| **Element** | **Mean** | **P95** | **Mean** | **P95** | **Mean** | **P95** | **Mean** | **P95** |
| **As** | 6.52 | 16.2 | 4.09 | 13.2 | 1.92 | 11.1 | 1.27 | 3.21 |
| **B** | 672 | 2024 | 326 | 1599 | 227 | 1297 | 40.7 | 102 |
| **Cu** | 6.24 | 23.6 | 4.22 | 16.9 | 3.45 | 10.4 | 78.8 | 356 |
| **Li** | 328 | 1115 | 415 | 1030 | 263 | 910 | 20.3 | 15.2 |
| **Mo** | 1.29 | 4.02 | 1.15 | 3.70 | 0.69 | 3.52 | 0.32 | 1.11 |
| **Ni** | 4.10 | 13.3 | 4.45 | 14.1 | 3.69 | 11.9 | 3.74 | 5.56 |
| **Pb** | 0.91 | 1.68 | 0.88 | 1.79 | 0.69 | 1.73 | 1.07 | 3.06 |
| **U** | 3.54 | 8.73 | 3.92 | 10 | 3.08 | 9.68 | 1.67 | 7.21 |
| **Zn** | 14.4 | 38.3 | 9.11 | 33.4 | 0.73 | 3.66 | 151 | 639 |

According to the results gathered in tab.9 the highest mean concentrations for all elements are usually found in the group “mineral waters of the world” and the lowest in German tap water. Exceptions are the elements Cu, Pb and Zn for which highest concentrations were found in German tap water. This indicates strongly an anthropogenic influence through contamination from installation materials.

Mean and P 95 values for the three "total dissolved matter" (TDS) groups, which are used in further calculations are given in tab.10.

Table 10: Mean and P 95 concentration of As, B, Cu, Li, Ni, Mo, Pb, U and Zn concentration in mineral waters of the world (µg/L) with low (TDS < 50 mg/L), medium (TDS 50 - 1000 mg/L) and high mineralisation (TDS > 1000 mg/L). Individual data and full descriptive statistics are collected in Knolle (2008)

| | Mineral waters of the world | | | | | |
|---|---|---|---|---|---|---|
| | low mineralisation | | medium mineralisation | | high mineralisation | |
| **Element** | **Mean** | **P 95** | **Mean** | **P 95** | **Mean** | **P 95** |
| **As** | 3.03 | 9.27 | 3.48 | 13.2 | 23.4 | 155 |
| **B** | 55.2 | 168 | 368 | 740 | 1719 | 9611 |
| **Cu** | 0.18 | 0.15 | 0.03 | 0.1 | 0.03 | 0.12 |
| **Li** | 5.01 | 19.6 | 4.77 | 17.3 | 10.5 | 33.8 |
| **Mo** | 17.4 | 73.9 | 65.2 | 310 | 1060 | 5000 |
| **Ni** | 0.7 | 3.99 | 1.10 | 3.85 | 3.24 | 6.83 |
| **Pb** | 3.9 | 10.9 | 3.51 | 13.2 | 7.13 | 26.6 |
| **U** | 0.95 | 1.38 | 0.94 | 1.85 | 0.86 | 3.09 |
| **Zn** | 1.45 | 6.3 | 1.23 | 6.24 | 7.54 | 15.7 |

According to the results gathered in tab.10 the highest mean concentrations for elements are usually found in mineral waters with a high mineralisation (TDS > 1000 mg/L). Exception is again Cu, which concentrations were higher in low mineralised waters. U concentrations seem to be more or less not affected by the mineralisation of water. The higher Cu concentrations may be an indication that waters with low mineralisation, at least when considered on a "world level" might be not pure well waters as stipulated within Germany by the Mineral and Table Water Ordinance (MTVO 2006), but mixtures with tap water, which according to tab. 10 is characterised by exceptional high Cu concentrations.

### 3.6 Original data and statistical methods

Due to the large size of the data sets the original data for this thesis are attached as SPSS data files. All statistical treatments were conducted with the SPSS 13.0 programme package. Levels of statistical significances are marked as follows: -- n.s. = not significant ($p > 0.05$); * = $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

# 4 Contribution of mineral and tap water to the dietary intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn by humans

This research work provides basic data from which many different scenarios of water drinking and dietary habits can be investigated for their effects on the daily intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn can be calculated. For each of these elements daily intakes are presented in the following subchapters whereby to some extend the structures of EFSA reportings was adopted.

The following tables will present means of As, B, Cu, Li, Mo, Ni, Pb, U and Zn exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn (µg/day) through dietary group types. These dietary group types are maintained at an energy input of 2000 kcal/day. Following EFSA procedures for the waters data for the occurrence means scenario and for the occurrence 95th percentile scenario are given. Water consumer types are grouped into “Tap water consumer” (TWC), “German bottled water consumer” (GBWC), “German and neighbours bottled water consumer” (NBWC), “World bottled water consumer” (WBWC), “Low mineralised bottled water consumer” (LMBWC), “Medium mineralised bottled water consumer” (MMBWC) and “High mineralised bottled water consumer” (HMBWC). Exposures were obtained by multiplying 2 L/day consumption by occurrence means or by the 95th percentile occurrence. Although 2 L of water are recommended from health organisations (Anonymous, 2010b; Mayo Clinic Staff, 2010) the average daily amount of tap and bottled water consumed is less than 1 L. However, adding to this the amount of water taken in statistically through water based beverages makes up to exactly this 2 L recommended (tab. 11):

The dietary groups are according to the definitions and structures given in chapter 3.3: “Standard”, “Vegetarian (ovo-lacto)”, “Vegan” and “Carnivore”. Values for dietary intake by different dietary group types are calculated from mean occurrence concentration (see table 8, chapter 3.4).

Table 11: Annual consumption of beverages in Germany (Sources: Websites and publications (2008 - 2010) from Unions of the Beverage Industries, the Federal Statistical Office, the Federal Agency for Agriculture and Food and Schulz et al. 2008)

| Beverage | Annual consumption per capita (L) | Natural water based (L) |
|---|---|---|
| Alcoholics | 146 | 116 |
| - beer | 116 | 116 |
| - wine | 20.1 | |
| - sparkling wine | 3.80 | |
| - spirits | 5.70 | |
| Non alcoholics | 297 | 238 |
| - bottled waters | 140 | 140 |
| - soft drinks | 117 | 76.4* |
| - juices | 39.8 | 21.8** |
| Hot and home drinks | 313 | 219 |
| - coffee | 148 | 148 |
| - tea | 70.9 | 70.9 |
| - milk | 91.3 | |
| Tap water | 183 | 183 |
| Total per capita | 939 | 756 |
| Daily per capita | 2.57 | 2.07 |

* 40.7 L of soft drinks are defitively made from deionised water (Coke drinks)

** 18.0 L fresh or direct squeezed juices

The contribution of drinking water to the daily element intake will be given for the means occurrence scenario. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) gives an idea to which extend a change of water drinking and dieting habits improvement in case of essential micronutrients.

## 4.1 Arsenic

Among the nine elements investigated in this research work As is the one which shows the largest range of daily element intakes among the four dietary group types. An ovo-lacto vegetarian diet supplies the smallest daily amount of As with solid food to the human body (50 µg/day) whereas a carnivore diet delivers 18.5 times as much as an ovo-lacto vegetarian diet (tab. 12).

The element As takes place 5 among the nine elements in terms of the concentration range in drinking waters. A tap water consumer would have the lowest (2.54 µg/day) but a consumer of high mineralised bottled water an 18.4 times higher input of As to the body (tab.12). The contribution of drinking water to the daily As intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 0.851 % with a range from 0.274 % for a tap water consuming carnivore to 4.83 % for a high mineralised bottled water consuming ovo-lacto vegetarian (tab. 12).

The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily As intake through a change of water drinking and dieting habits is -94.6 %.

Table 12: Means of arsenic exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of As (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 2.54 | 6.42 |
| | | |
| 2 German bottled water consumer (GBWC) | 3.84 | 22.2 |
| 3 German and neighbours bottled water consumer (NBWC) | 8.18 | 24.2 |
| 4 World bottled water consumer (WBWC) | 13.0 | 32.4 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 4.07 | 18.5 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 4.96 | 26.4 |
| 7 High mineralised bottled water consumer (HMBWC) | 46.8 | 310 |
| | | |
| **Dietary group type *** | | |
| Standard | 296 | |
| Vegetarian (ovo-lacto) | 50 | |
| Vegan | 67 | |
| Carnivore | 925 | |
| | | |
| **Daily intake** | | |
| Lowest daily As intake (water consumer + dietary group type combination) | 1 + Vegetarian (ovo-lacto) | |
| Lowest daily As intake (µg/day) | 52.5 | |
| Contribution of water (%) to the daily intake of As at lowest intake scenario | 4.77 | |
| Maximum daily As intake (water consumer + dietary group type combination) | 7 + Carnivore | 7 + Carnivore |
| Maximum daily As intake (µg/day) | 972 | 1,235 |
| Maximum contribution of water (%) to the daily intake of As at type combination | 4.82 | 25.1 |

Remarks: Scenario A: As exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: As exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean As occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.2 Boron

Among the nine elements investigated in this research work B shows the second largest range of daily element intakes among the four dietary group types. A carnivore diet supplies the smallest amount of B with solid food to the human body (2460 µg/day) whereas a vegan diet delivers 3.8 times as much as a carnivore diet. The element B takes place 3 among the nine elements in terms of the concentration range in drinking waters. A tap water consumer would have the lowest (81.4 µg/day) but a consumer of high mineralised bottled water a 42.2 times higher input of B to the body (tab. 13).

The contribution of drinking water to the daily B intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 2.21 % with a range from 1.06 % for a tap water consuming vegan to 58.3 % for a high mineralised bottled water consuming carnivore. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily B intake through a change of water drinking and dieting habits is -76.9 % (tab. 13).

Table 13: Means of boron exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of B (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 81.4 | 204 |
| | | |
| 2 German bottled water consumer (GBWC) | 455 | 2,594 |
| 3 German and neighbours bottled water consumer (NBWC) | 653 | 3,198 |
| 4 World bottled water consumer (WBWC) | 1,343 | 4,049 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 110 | 336 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 736 | 1,480 |
| 7 High mineralised bottled water consumer (HMBWC) | 3,438 | 19,222 |
| | | |
| **Dietary group type *** | | |
| Standard | 3,610 | |
| Vegetarian (ovo-lacto) | 4,990 | |
| Vegan | 7,580 | |
| Carnivore | 2,460 | |
| | | |
| **Intake** | | |
| Lowest daily B intake (water + dietary group type combination) | 1 + Vegan | |
| Lowest daily B intake (µg/day) | 2,541 | |
| Contribution of water (%) to the daily intake of B at lowest intake scenario | 3.20 | |
| Maximum daily B intake (water consumer + dietary group type combination) | 7 + Vegan | 7 + Vegan |
| Maximum daily B intake (µg/day) | 11,018 | 26,802 |
| Maximum contribution of water (%) to the daily intake of B at type combination | 31.2 | 71.7 |

Remarks: Scenario A: B exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: B exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean B occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.3 Copper

Among the nine elements investigated in this research work Cu shows the third largest range of daily element intakes among the four dietary group types. An ovo-lacto vegetarian diet supplies the smallest amount of Cu with solid food to the human body (2,340 µg/day) whereas a carnivore diet delivers 2.7 times as much as an ovo-lacto vegetarian diet. The element Cu takes place 4 among the nine elements in terms of the concentration range in drinking waters. A consumer of German bottled waters would have the lowest (6.9 µg/day) but a consumer of German tap water a 22.9 times higher input of Cu to the body (tab. 14).

The contribution of drinking water to the daily Cu intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 4.65 % with a range from 0.130 % for a German bottled water or high mineralised bottled water consuming carnivore to 6.33 % for a tap water consuming ovo-lacto vegetarian. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Cu intake through a change of water drinking and dieting habits is -61.9 %.

Table 14: Means of copper exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Cu (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 158 | 711 |
| | | |
| 2 German bottled water consumer (GBWC) | 6.9 | 20.8 |
| 3 German and neighbours bottled water consumer (NBWC) | 8.4 | 33.8 |
| 4 World bottled water consumer (WBWC) | 12.5 | 47.2 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 10.0 | 39.2 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 9.54 | 34.6 |
| 7 High mineralised bottled water consumer (HMBWC) | 21.0 | 67.2 |
| | | |
| **Dietary group type *** | | |
| Standard | 3,240 | |
| Vegetarian (ovo-lacto) | 2,340 | |
| Vegan | 3,290 | |
| Carnivore | 6,390 | |
| | | |
| **Intake** | | |
| Lowest daily Cu intake (water consumer + dietary group type combination) | 2 + Vegetarian (ovo-lacto) | |
| Lowest daily Cu intake (µg/day) | 2498 | |
| Contribution of water (%) to the daily intake of Cu at lowest intake scenario | 6.33 | |
| Maximum daily Cu intake (water consumer + dietary group type combination) | 1 + Carnivore | 1 + Carnivore |
| Maximum daily Cu intake (µg/day) | 6,548 | 7,101 |
| Maximum contribution of water (%) to the daily intake of Cu at type combination | 2.40 | 10.0 |

Remarks: Scenario A: Cu exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Cu exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Cu occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.4 Lithium

Among the nine elements investigated in this research work Li shows the fifth largest range of daily element intakes among the four dietary group types. A carnivore diet supplies the smallest amount of Li with solid food to the human body (96 µg/day) whereas a vegan diet delivers 2 times as much as a carnivore diet. The element Li takes the second place among the nine elements in terms of the concentration range in drinking waters. A consumer of German tap water would have the lowest (40.6 µg/day) but a consumer of high mineralised bottled waters a 52.2 times higher input of Li to the body (tab. 15).

The contribution of drinking water to the daily Li intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 24.1 % with a range from 15.2 % for a low mineralised bottled water consuming vegan to 95.7 % for a high mineralised bottled water consuming carnivore. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Li intake through a change of water drinking and dieting habits is -94.3 %.

Table 15: Means of lithium exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Li (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 40.6 | 30.4 |
| | | |
| 2 German bottled water consumer (GBWC) | 526 | 1,820 |
| 3 German and neighbours bottled water consumer (NBWC) | 830 | 2,060 |
| 4 World bottled water consumer (WBWC) | 655 | 2,230 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 34.8 | 146 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 130 | 620 |
| 7 High mineralised bottled water consumer (HMBWC) | 2,120 | 10,000 |
| | | |
| **Dietary group type *** | | |
| Standard | 128 | |
| Vegetarian (ovo-lacto) | 146 | |
| Vegan | 194 | |
| Carnivore | 96 | |
| | | |
| **Intake** | | |
| Lowest daily Li intake (water consumer + dietary group type combination) | 5 + Carnivore | |
| Lowest daily Li intake (µg/day) | 131 | |
| Contribution of water (%) to the daily intake of Li at lowest intake scenario | 26.6 | |
| Maximum daily Li intake (water consumer + dietary group type combination) | 7 + Vegan | 7 + Vegan |
| Maximum daily Li intake (µg/day) | 2314 | 10194 |
| Maximum contribution of water (%) to the daily intake of Li at type combination | 91.6 | 98.1 |

Remarks: Scenario A: Li exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Li exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Li occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.5 Molybdenum

Among the nine elements investigated in this research work Mo shows the seventh largest range of daily element intakes among the four dietary group types. A carnivore diet supplies the smallest amount of Mo with solid food to the human body (425 µg/day) whereas a vegan diet delivers 1.7 times as much as a carnivore diet. The element Mo takes the sixth place among the nine elements in terms of the concentration range in drinking waters. A consumer of German tap water would have the lowest (0.646 µg/day) but a consumer of high mineralised bottled waters a 6.9 times higher input of Mo to the body (tab. 16).

The contribution of drinking water to the daily Mo intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 0.150 % with a range from 0.091 % for a tap water consuming vegan to 1.04 % for a high mineralised bottled water consuming carnivore. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Mo intake through a change of water drinking and dieting habits is -40.1 %.

Table 16: Means of molybdenum exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Mo (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 0.646 | 2.22 |
| | | |
| 2 German bottled water consumer (GBWC) | 1.39 | 5.04 |
| 3 German and neighbours bottled water consumer (NBWC) | 2.30 | 7.40 |
| 4 World bottled water consumer (WBWC) | 2.58 | 8.04 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 1.40 | 5.98 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 2.20 | 7.70 |
| 7 High mineralised bottled water consumer (HMBWC) | 4.48 | 13.7 |
| | | |
| **Dietary group type *** | | |
| Standard | 429 | |
| Vegetarian (ovo-lacto) | 499 | |
| Vegan | 706 | |
| Carnivore | 425 | |
| | | |
| **Intake** | | |
| Lowest daily Mo intake (water consumer + dietary group type combination) | 1 + Carnivore | |
| Lowest daily Mo intake (µg/day) | 426 | |
| Contribution of water (%) to the daily intake of Mo at lowest intake scenario | 0.152 | |
| Maximum daily Mo intake (water consumer + dietary group type combination) | 7 + Vegan | 7 + Vegan |
| Maximum daily Mo intake (µg/day) | 711 | 720 |
| Maximum contribution of water (%) to the daily intake of Mo at type combination | 0.631 | 1.90 |

Remarks: Scenario A: Mo exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Mo exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Mo occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.6 Nickel

Among the nine elements investigated in this research work Ni shows the fourth largest range of daily element intakes among the four dietary group types. A carnivore diet supplies the smallest amount of Ni with solid food to the human body (268 µg/day) whereas a vegan diet delivers 2.3 times as much as a carnivore diet. The element Ni takes the eighth place among the nine elements in terms of the concentration range in drinking waters. A consumer of German tap water would have the lowest (5.48 µg/day) but a consumer of high mineralised bottled waters a 2.6 times higher input of Ni to the body (tab. 17).

The contribution of drinking water to the daily Ni intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 1.57 % with a range from 0.517 % for a tap water consuming vegan to 5.07 % for a high mineralised bottled water consuming carnivore. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Ni intake through a change of water drinking and dieting habits is -57.0 %.

Table 17: Means of nickel exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Ni (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 5.48 | 11.1 |
| | | |
| 2 German bottled water consumer (GBWC) | 7.38 | 23.8 |
| 3 German and neighbours bottled water consumer (NBWC) | 8.90 | 28.2 |
| 4 World bottled water consumer (WBWC) | 8.20 | 26.6 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 5.80 | 21.8 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 7.02 | 24.4 |
| 7 High mineralised bottled water consumer (HMBWC) | 14.3 | 53.2 |
| | | |
| **Dietary group type *** | | |
| Standard | 343 | |
| Vegetarian (ovo-lacto) | 427 | |
| Vegan | 625 | |
| Carnivore | 268 | |
| | | |
| **Intake** | | |
| Lowest daily Ni intake (water consumer + dietary group type combination) | 1 + Carnivore | |
| Lowest daily Ni intake (µg/day) | 275 | |
| Contribution of water (%) to the daily intake of Ni at lowest intake scenario | 2.68 | |
| Maximum daily Ni intake (water consumer + dietary group type combination) | 7 + Vegan | 7 + Vegan |
| Maximum daily Ni intake (µg/day) | 639 | 678 |
| Maximum contribution of water (%) to the daily intake of Ni at type combination | 2.23 | 7.84 |

Remarks: Scenario A: Ni exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Ni exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Ni occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.7 Lead

Among the nine elements investigated in this research work Pb shows the sixth largest range of daily element intakes among the four dietary group types. A carnivore or standard diet supplies the smallest amount of Pb with solid food to the human body (112 µg/day) whereas a vegan diet delivers 1.7 times as much as a carnivore or standard diet. The element Pb takes the last place among the nine elements in terms of the concentration range in drinking waters. A consumer of German bottled waters would have the lowest (1.38 µg/day) but a consumer of German tap water a 1.6 times higher input of Pb to the body (tab. 18).

The contribution of drinking water to the daily Pb intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 1.89 % with a range from 0.679 % for a German bottled water consuming vegan to 1.89 % for a tap water and standard diet consuming individual. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Pb intake through a change of water drinking and dieting habits is -33.1 %.

Table 18: Means of lead exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Pb (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 2.14 | 6.12 |
| | | |
| 2 German bottled water consumer (GBWC) | 1.38 | 3.46 |
| 3 German and neighbours bottled water consumer (NBWC) | 1.76 | 3.58 |
| 4 World bottled water consumer (WBWC) | 1.81 | 3.36 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 1.90 | 2.76 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 1.88 | 3.70 |
| 7 High mineralised bottled water consumer (HMBWC) | 1.72 | 4.18 |
| | | |
| **Dietary group type *** | | |
| Standard | 111 | |
| Vegetarian (ovo-lacto) | 137 | |
| Vegan | 202 | |
| Carnivore | 112 | |
| | | |
| **Intake** | | |
| Lowest daily Pb intake (water consumer + dietary group type combination) | 2 + Standard | |
| Lowest daily Pb intake (µg/day) | 112 | |
| Contribution of water (%) to the daily intake of Pb at lowest intake scenario | 0.051 | |
| Maximum daily Pb intake (water consumer + dietary group type combination) | 1 + Vegan | 1 + Vegan |
| Maximum daily Pb intake (µg/day) | 204 | 208 |
| Maximum contribution of water (%) to the daily intake of Pb at type combination | 1.06 | 2.94 |

Remarks: Scenario A: Pb exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Pb exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Pb occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.8 Uranium

Among the nine elements investigated in this research work U shows the smallest range of daily element intake among the four dietary group types. An ovo-lacto vegetarian diet supplies the smallest amount of U with solid food to the human body (1.46 µg/day) whereas a carnivore diet delivers only 1.4 times as much as an ovo-lacto vegetarian diet. The element U takes the seventh place among the nine elements in terms of the concentration range in drinking waters. A consumer of German tap or low mineralised bottled waters would have the lowest (2.9 µg/day) but a consumer of high mineralised bottled waters a 5.2 times higher input of U to the body (tab. 19).

The contribution of drinking water to the daily U intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 64.7 % with a range from 58.1 % for a tap or low mineralised bottled water consuming carnivore to 91,2 % for a high mineralised bottled water consuming ovo-lacto vegetarian. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily U intake through a change of water drinking and dieting habits is -75.4 %.

Table 19: Means of uranium exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of U (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 2.90 | 16.0 |
| | | |
| 2 German bottled water consumer (GBWC) | 6.16 | 19.4 |
| 3 German and neighbours bottled water consumer (NBWC) | 5.84 | 20.0 |
| 4 World bottled water consumer (WBWC) | 5.08 | 17.5 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 2.90 | 12.6 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 2.46 | 12.5 |
| 7 High mineralised bottled water consumer (HMBWC) | 15.1 | 31.4 |
| | | |
| **Dietary group type *** | | |
| Standard | 1.58 | |
| Vegetarian (ovo-lacto) | 1.46 | |
| Vegan | 1.96 | |
| Carnivore | 2.09 | |
| | | |
| **Intake** | | |
| Lowest daily U intake (water consumer + dietary group type combination) | 1 + Vegetarian (ovo-lacto) | |
| Lowest daily U intake (µg/day) | 4.36 | |
| Contribution of water (%) to the daily intake of U at lowest intake scenario | 66.6 | |
| Maximum daily U intake (water consumer + dietary group type combination) | 7 + Carnivore | 7 + Carnivore |
| Maximum daily U intake (µg/day) | 17.7 | 33.5 |
| Maximum contribution of water (%) to the daily intake of U at type combination | 87.8 | 93.8 |

Remarks: Scenario A: U exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: U exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean U occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

## 4.9 Zinc

Among the nine elements investigated in this research work Zn shows the second smallest range of daily element intakes among the four dietary group types after U. An ovo-lacto vegetarian diet supplies the smallest amount of Zn with solid food to the human body (11,300 µg/day) whereas a carnivore diet delivers only 1.5 times as much as an ovo-lacto vegetarian diet. But the element Zn takes the first place among the nine elements in terms of the concentration range in drinking waters. A consumer of German bottled waters would have the lowest (1.46 µg/day) but a consumer of German tap water 207 times higher input of Zn to the body (tab. 20).

The contribution of drinking water to the daily Zn intake (at means occurrence scenario for a tap water drinking standard diet consumer) is 2.40 % with a range from 0.04 % for German bottled water consuming carnivore to 0.674 % for a tap water consuming ovo-lacto vegetarian. The maximum reduction potential (relative difference between highest and lowest daily input water consumer + dietary group type combination at means occurrence scenario) for the daily Zn intake through a change of drinking and dieting habits is -33.1 %.

Table 20: Means of zinc exposure estimates (µg/day) in different water consumer types according to different exposure scenarios compared to the average daily intake of Zn (µg/day) through dietary group types (maintained at an energy input of 2000 kcal/day)

| | **Scenario** | |
|---|---|---|
| | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| **Water consumer type** | | |
| 1 Tap water consumer (TWC) | 302 | 1277 |
| | | |
| 2 German bottled water consumer (GBWC) | 1.46 | 5.32 |
| 3 German and neighbours bottled water consumer (NBWC) | 18.2 | 64.8 |
| 4 World bottled water consumer (WBWC) | 28.8 | 76.6 |
| | | |
| 5 Low mineralised bottled water consumer (LMBWC) | 30.1 | 53.2 |
| 6 Medium mineralised bottled water consumer (MMBWC) | 19.3 | 53.4 |
| 7 High mineralised bottled water consumer (HMBWC) | 47.4 | 182 |
| | | |
| **Dietary group type *** | | |
| Standard | 12,300 | |
| Vegetarian (ovo-lacto) | 11,300 | |
| Vegan | 12,700 | |
| Carnivore | 16,600 | |
| | | |
| **Intake** | | |
| Lowest daily Zn intake (water consumer + dietary group type combination) | 2 + Vegetarian (ovo-lacto) | |
| Lowest daily Zn intake (µg/day) | 11,301 | |
| Contribution of water (%) to the daily intake of Zn at lowest intake scenario | 0.013 | |
| Maximum daily Zn intake (water consumer + dietary group type combination) | 1 + Carnivore | 1 + Carnivore |
| Maximum daily Zn intake (µg/day) | 16902 | 17877 |
| Maximum contribution of water (%) to the daily intake of Zn at type combination | 1.79 | 7.14 |

Remarks: Scenario A: Zn exposure obtained by multiplying 2 L/day consumption by occurrence means (see Tab. 9 & 10, chapter 3.5)

Remarks: Scenario B: Zn exposure obtained by multiplying 2 L/day consumption by 95th percentile occurrence (see Tab. 9 & 10, chapter 3.5)

* Values for dietary intake by different dietary group types are calculated from mean Zn occurrence concentration (see Tab. 6 & 7, chapter 3.3, and Tab. 8, chapter 3.4)

# 5 Human exposure assessment for the elements As, B, Cu, Li, Mo, Ni, Pb, U and Zn

## 5.1 Exposure of German population to As, B, Cu, Li, Mo, Ni, Pb, U and Zn in tap waters

In the following chapter the exposure of German population in tap waters is assessed. Such an assessment is only possible for tap waters and not for mineral waters as detailed data for the consumption of individual mineral water brands are not available or not revealed to the public by the mineral water industry.

The data of the tap water samples are geocoded and can thus be presented as maps over the entire country. They do, however, not image the geological background causing the concentrations. There are two main reasons for this: firstly, the geographical location of the waterworks might be far away from the consumers tap where the sample and the geographical coordinates were taken and secondly the differences in the catchment of the water e.g. from reservoirs, rivers and their beds or wells of different depth and access to different aquifers. The evaluation of the geological background of the geographical distribution of element concentrations in tap waters were not task of this research work but can be found particularly for U in the work of Knolle (2008) and Birke et al. (2008) or, for As, B, Cu, Li, Mo, Ni, Pb and Zn is the objective of ongoing and future research projects (Jacobs 2012).

A new and unique approach of the research work reported here is the linking of concentration data in drinking water to the number of individuals who consumes this water (see chapter 3.1). From this data the percentage of persons of the total population for distinctive concentration classes was calculated and is designated in the following text as the “percentage of population exposed”. This provides far more exact information on exposures than just a simple frequency analysis of the numbers of samples to concentrations.

Furthermore the element concentration in the waters has been correlated with the percentage of population represented by each sample which shall indicate to certain extend the risk of exposure depending on the size of the water supply unit. This information may be, however, biased by a number of other factors which will be discussed for each element separately if necessary.

The tables displaying the exposure of the German population to As, B, Cu, Li, Mo, Ni, Pb, U and Zn in tap water show for individual concentration classes the percentage of samples of the entire number of samples taken and the % of the total population exposed of the total population represented by all samples. The division of concentration classes starts with the samples with concentrations below the detection limit (see chapter 3.2) and comprises as far

as available critical thresholds given in the relevant literature. Beside this two all other concentration classes are arbitrary.

### 5.1.1 Arsenic

Tab. 21 displays the exposure of German population to As in tap water. A quarter of the samples showed As concentration below the detection limit, but this concentration class comprises already nearly half of the entire population. Just looking at the percentage of samples in this concentration class would distinctively underestimate the size of the population with access to virtually As free tap water, but at the same time overestimate the the exposure to higher As concentrations. As is considered as one of the most serious contaminant with a high potential to harm human health (EFSA 2009). As concentrations higher than the threshold value of the German ordinance for drinking water (TrinkV 2010) were only found in 0.2 % of the samples comprising a population exposed of less than 0.03 % (tab. 21). In absolute values this were only two sources, one in Baden-Baden an unusual tap source with general access to the public ("Kurbrunnen") and an extreme As concentration of 250 µg/L As and a source in Bad Bergzabern with much lower, but still with an exceptionally high concentration of 12.3 µg/L As.

Table 21: Exposure of German population to As in tap water (% of samples of the entire number of samples taken (n = 750) and the % of the population exposed of the total population observed (n = 29,551,132))

| **Concentration of As (µg/L)** | **Percentage** | |
|---|---|---|
| | **of samples** | **of population exposed** |
| < LLD * | 27.6 | 41.0 |
| LLD – 2 | 61.3 | 54.8 |
| 2 – 5 | 9.10 | 3.84 |
| 5 – 10 | 1.70 | 0.41 |
| 10 – 20** | 0.10 | 0.03 |
| > 20 ** | 0.10 | 0.00 |

* LLD = Lower limit of detection
** Above maximum permissible value according to TrinkwV (2011)

If one considers element concentrations in low mineralised mineral waters (tab. 10, chapter 3.5) as some sort of a natural background concentration tap water concentrations exceeding the range of concentrations in mineral waters might be an indication for anthropogenic influences. With an average of 1.27 µg/L the As concentration were well below the

concentration in mineral waters of German origin (1.92 µg/L As, Tab. 9, chapter 3.5) giving no lead to anticipate anthropogenic alterations of the As concentrations in tap water.

The As concentration in the tap water samples showed a significant ($p < 0.05$) and positive correlation to B (0.698) and Li (0.998) which says that increasing exposure to As comes along with an increasing exposure to B and Li.

A scattergram of As concentration in tap water with the % of the population exposed of the total population observed (fig. 5) reveals a pattern which was found for most of the other elements: the exposure to As increases exponentially with the decrease of the corresponding population size associated with a sample. There may be different reasons behind this phenomenon, but the main one is certainly the fact that in larger water works more different water sources are mixed which may dilute a single distinctively high As loaded water.

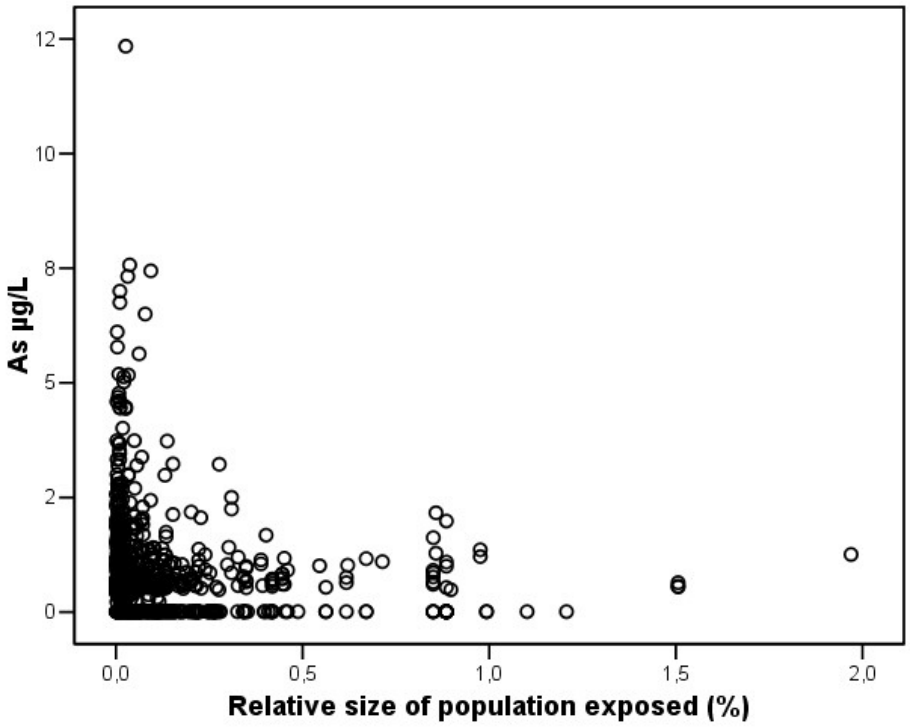


Figure 5: Arsenic concentration in 750 German tap water samples and % of the population exposed of the total population observed (n = 29,551,132). The extreme value of 250 µg/L As found in a source in Baden-Baden has been excluded in this figure

The regional distribution of As concentrations in German tap water are shown in fig. 16 in the annex to this work.

### 5.1.2 Boron

Tab. 22 displays the exposure of German population to B in tap water. Only 7 % of the samples investigated, representing 3.21 % of the population covered had B concentrations below the lower limit of detection. The majority, which is three quarters of the samples and of the population covered fall below a concentration below 50 µg/L B.

Table 22: Exposure of German population to B in tap water (% of samples of the entire number of samples taken (n = 458) and the % of the population exposed of the total population observed (n = 27,242,389))

| Concentration of B (µg/L) | Percentage | |
|---|---|---|
| | of samples | of population exposed |
| < LLD* | 7.00 | 3.21 |
| LLD – 50 | 71.2 | 62.4 |
| 50 – 500 | 21.2 | 34.4 |
| > 1000 ** | 0.70 | 0.01 |

* LLD = Lower limit of detection
** Above maximum permissible value according to TrinkwV (2010), critical value for groundwater is 190 µg/L (GrwV 2010)

The German ordinance for drinking water assigns maximum permissible concentration of 1000 µg/L B which is met or exceeded by only 0.7 % of the samples covering only 0.01 % of the population. A fifth of the samples covering a third of the population fell in the concentration range between 50 and 500 µg/L. Within this class were two samples above 190 µg/L B which is the assigned critical value for groundwater (GrwV 2010).
The reason for the remarkable difference between the 1000 µg/L B as permissible value according to the drinking water ordinance and the much lower value of 190 µg/L B as critical value for groundwater is that the first reflects of toxicological phenomenon which may occur with the ingestion of waters with that high B concentrations but the lower value for groundwater is meant as an indicator for anthropogenic influences (Knolle 2008). Table 2 (chapter 1) reminds that with an annual load of 1,575 T B through mineral P fertilisers alone, agriculture is one of the significant contributors to man-made environmental B pollution.

With an average of 40.7 µg/L the B concentration in the tap waters were well below the concentration in mineral waters of German origin (227 µg/L B, tab. 9, chapter 3.5) giving no lead to anticipate anthropogenic alterations of the B concentrations in tap water.
The B concentration in the tap water samples showed a significant ($p < 0.05$) high (0.713) positive correlation to the Li concentration. The correlations to Mo, Ni and U concentrations

were much looser (0.373, 0.141 and 0.110) but still significant ($p < 0,05$).

Although less clearer a scattergram of B concentration in tap water with the % of the population exposed of the total population observed (fig. 6) reveals to some extend a similar pattern already found with As (fig. 5), which says that smaller supply systems show a tendency to deliver water with higher B concentrations.

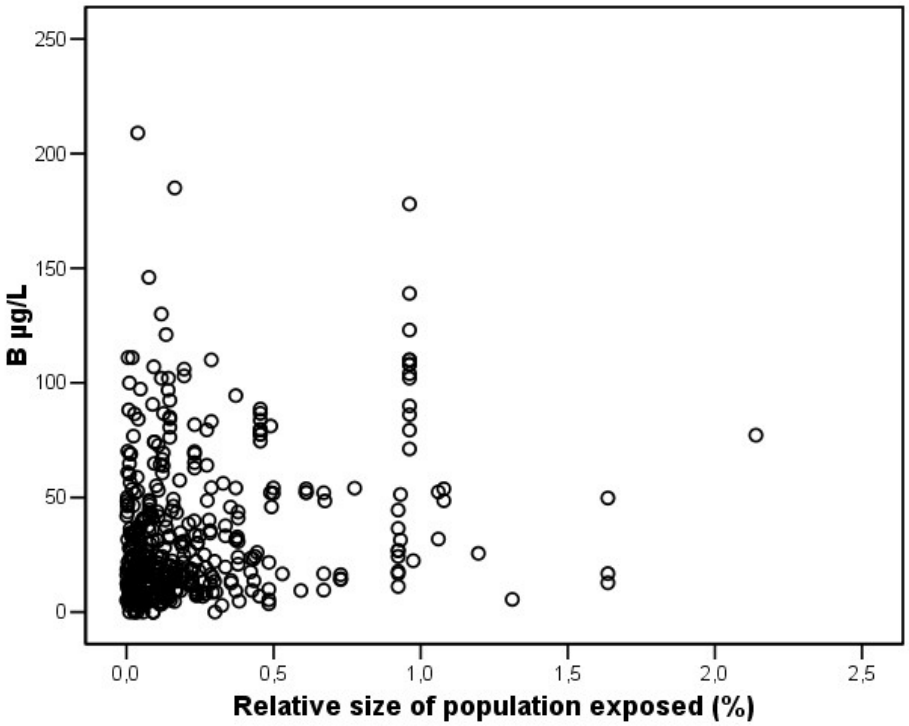


Figure 6: Boron concentration in 458 German tap water samples and % of the population exposed of the total population observed (n = 27,242,389)

The regional distribution of B concentrations in German tap water are shown in fig. 17 in the annex to this work.

### 5.1.3 Copper

Tab. 23 displays the exposure of German population to Cu in tap water. The majority of the samples and also the majority of the population covered by this investigation showed exposure to Cu concentrations below the lower limit of detection for Cu (68.9 % and 56.5 % respectively).

Table 23: Exposure of German population to Cu in tap water (% of samples of the entire number of samples taken (n = 750) and the % of the population exposed of the total population observed (n = 29,551,132))

| **Concentration of Cu (µg/L)** | **Percentage** | |
|---|---|---|
| | **of samples** | **of population exposed** |
| < LLD* | 68.9 | 56.5 |
| LLD – 100 | 13.9 | 18.3 |
| 100 – 1,000 | 16.4 | 24.2 |
| 1,000 – 2,000 | 0.50 | 0.97 |
| > 2,000 ** | 0.30 | 0.01 |

*LLD = Lower limit of detection
**Above maximum permissible value according to TrinkwV (2011) (critical value for groundwater is 14 µg/L (GrwV 2010)

The German ordinance for drinking water assigns maximum permissible concentration of 2000 µg/L Cu which is met or exceeded by only 0.3 % of the samples covering only 0.01 % of the population. Again the German ordinance for groundwater sets the threshold value for Cu in groundwater much lower at 14 µg/L Cu (GrwV 2010). Applying this value to the data set reveals that 58.4 % of the samples covering 68.7 % of the population are exposed to drinking water with Cu concentrations below the maximum permissible value according to the drinking water ordinance but exceeding the threshold value for groundwater. Like with B the reason for the remarkable difference between the critical values in both ordinances are that the higher one reflects on toxicological phenomena which may occur with the ingestion of waters with high Cu concentrations but the lower value for groundwater is meant as an indicator for anthropogenic influences (FAL 2007). Unclear is however, if this anthropogenic source is to be addressed as plumbing material or from extensive discharge of Cu to which also agriculture (see tab. 2, chapter 1) contributes.

With an average of 78.8 µg/L the Cu concentrations in the tap waters were high above the concentration in mineral waters of German origin (3.45 µg/L Cu, Tab. 9, chapter 3.5) which strongly indicates anthropogenic sources contributing largely to the Cu concentrations in drinking water. The strong anthropogenic background might also be the reason for the, although significant ($p < 0.05$), but very weak correlation of the Cu concentrations with only Mo (0.280) and U (-0.098).

Although even less clearer than the with B a scattergram of Cu concentration in tap water with the % of the population exposed of the total population observed (fig. 7) reveals to some extend a similar pattern already found with As and B (figs. 5 & 6), which says that smaller supply systems show a tendency to deliver water with higher Cu concentrations.

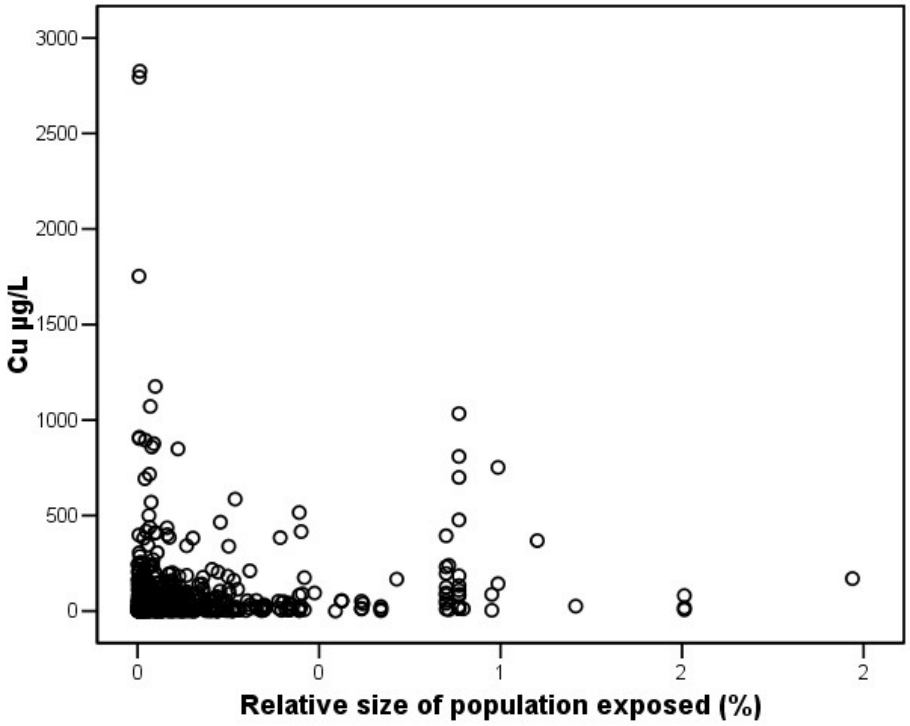


Figure 7: Cu concentration in 750 German tap water samples and % of the population exposed of the total population observed (n = 29,551,132)

This result is confirmed by the Schulz et al. (2008) who found in privately operated water supplies more frequently higher Cu concentrations in tap water.

The regional distribution of Cu concentrations in German tap water are shown in fig. 18 in the annex to this work.

### 5.1.4 Lithium

Tab. 24 displays the exposure of German population to Li in tap water. The numbers of samples and percentages of covered population are much more even distributed over the entire range of Li concentrations than for any other element considered in this study.
Although Li is an element with pharmaceutical significance no critical value for this element

can be found in the literature. Considering the relation of Li to Na in the blood serum being 345:1 and a limit value of 200,000 µg/L Na in the German drinking water ordinance (TrinkwV 2011) a limit for Li in drinking water of around 580 µg/L Li could be anticipated. Only one sample in the entire data set exceed this value and this sample was again the one from Baden-Baden ("Kurbrunnen") to which the public has free access, but which might not been considered as a typical tap water.

Table 24: Exposure of German population to Li in tap water (% of samples of the entire number of samples taken (n = 458) and the % of the population exposed of the total population observed (n = 27,242,389))

| **Concentration of Li (µg/L)** | **Percentage** | |
|---|---|---|
| | **of samples** | **of population exposed** |
| LLD* | 25.3 | 21.7 |
| LLD – 2 | 12.9 | 8.38 |
| 2 – 5 | 29.5 | 29.4 |
| 5 – 10 | 21.0 | 31.7 |
| 10 – 580 | 11.1 | 8.87 |
| > 580 | 0.20 | 0.02 |

* LLD = Lower limit of detection

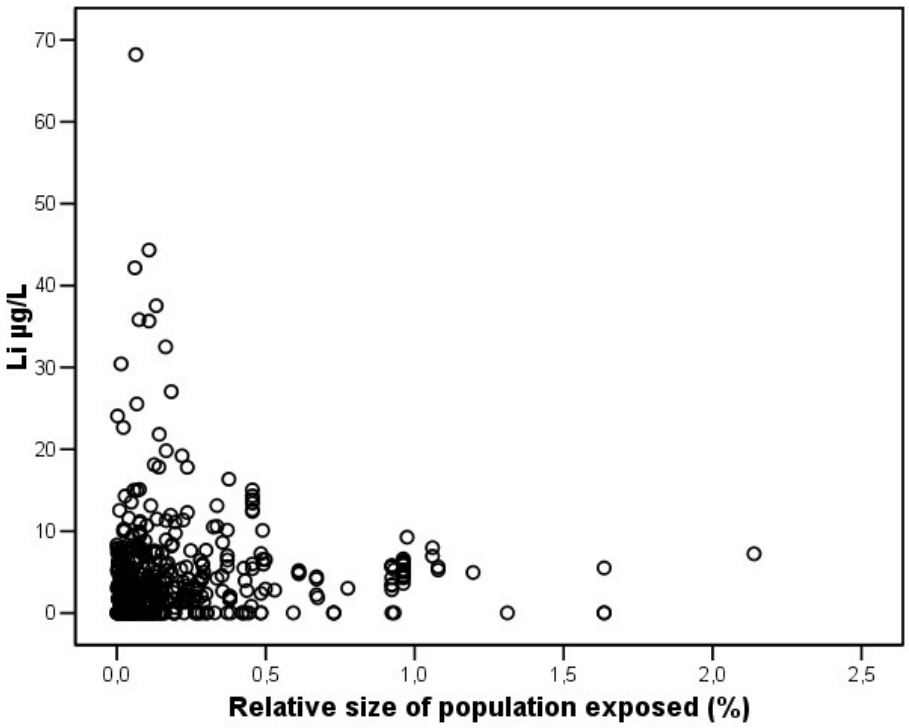


Figure 8: Li concentration in 458 German tap water samples and % of the population exposed of the total population observed (n = 27,242,389).

With an average of 20.3 µg/L the Li concentration in German tap waters were well below the concentrations in mineral waters of German origin (263 µg/L Li, tab. 9, chapter 3.5) giving no lead to anticipate anthropogenic alterations of the Li concentrations in tap water.

The Li concentration in the tap water samples showed a significant ($p < 0.05$) high (0.998 and 0.713) positive correlation to the As and B concentrations indicating that also the exposure to this elements increases with each of them.

A scattergram of Li concentrations in tap water with the % of the population exposed of the total population observed (fig. 8) revealed a very similar pattern already found with As (fig. 5), which says that smaller supply systems show a tendency to deliver water with higher Li concentrations.

The regional distribution of Li concentrations in German tap water are shown in fig. 19 in the annex to this work.

### 5.1.5 Molybdenum

Tab. 25 displays the exposure of German population to Mo in tap water. The numbers of samples and the percentages of population covered show a maximum around 0.25 - 0.50 µg/L Mo. Even the highest Mo concentrations found in German tap waters are far lower than the maximum permissible value according to WHO (2006) which is 70 µg/L.

Table 25: Exposure of German population to Mo in tap water (% of samples of the entire number of samples taken (n = 458) and the % of the population exposed of the total population observed (n = 27,242,389))

| **Concentration of Mo (µg/L)** | **Percentage** | |
|---|---|---|
| | **of samples** | **of population exposed** |
| < 0.10 | 51.3 | 41.0 |
| 0.10 – 0.25 | 7.20 | 6.00 |
| 0.25 – 0.50 | 17.2 | 20.5 |
| 0.50 – 0.75 | 8.30 | 14.6 |
| > 0.75 | 15.9 | 17.9 |

With an average of 0.32 µg/L the Mo concentrations in German tap waters are well below the concentrations in mineral waters of German origin (0.69 µg/L Mo, tab. 9, chapter 3.5) giving no lead to anticipate anthropogenic alterations of the Mo concentrations in tap water.
The Mo concentrations in the tap water samples showed a significant ($p < 0.05$) but only weak correlations to the Ni (0.255), U (0.138) and Zn (0.147) concentrations.

A scattergram of Mo concentrations in tap water with the % of the population exposed of the total population observed (fig. 9) revealed a much weaker correlation between the element concentrations and the size of the supply system than found with the elements discussed before.

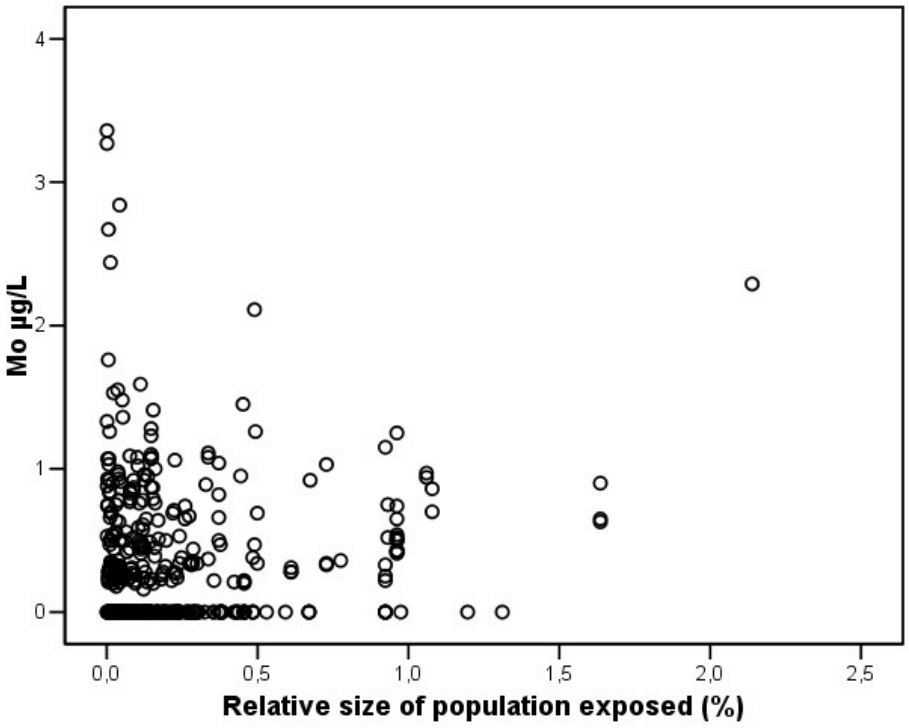


Figure 9: Mo concentration in 458 German tap water samples and % of the population exposed of the total population observed (n = 27,242,389).

The regional distribution of Mo concentrations in German tap water are shown in fig. 20 in the annex to this work.

### 5.1.6 Nickel

Tab. 26 displays the exposure of German population to Ni in tap water. Ni is considered as toxic element but more than 98 % of all samples and also of the population covered were related to Ni concentrations well beyond the maximum permissible value of 20 µg/L Ni according to the German drinking water ordinance (TrinkwV 2011). Still one third of the population observed had access to water with Ni concentrations below the lower limit of detection.

Table 26: Exposure of German population to Ni in tap water (% of samples of the entire number of samples taken (n = 750) and the % of the population exposed of the total population observed (n = 29,551,132))

| Concentration of Ni (µg/L) | Percentage | |
|---|---|---|
| | of samples | of population exposed |
| < LLD* | 31.7 | 28.3 |
| LLD – 2 | 49.6 | 49.1 |
| 2 – 5 | 12.7 | 15.2 |
| 5 – 10 | 3.20 | 4.66 |
| 10 – 20 | 1.10 | 1.63 |
| > 20 ** | 1.70 | 1.07 |

* LLD = Lower limit of detection
** Above maximum permissible value according to TrinkwV (2011)

With an average of 2.74 µg/L the Ni concentrations in German tap waters are still below the concentrations in mineral waters of German origin (3.69 µg/L Ni, tab. 9, chapter 3.5) which again gives no lead to anticipate anthropogenic alterations of the Ni concentrations in tap water.

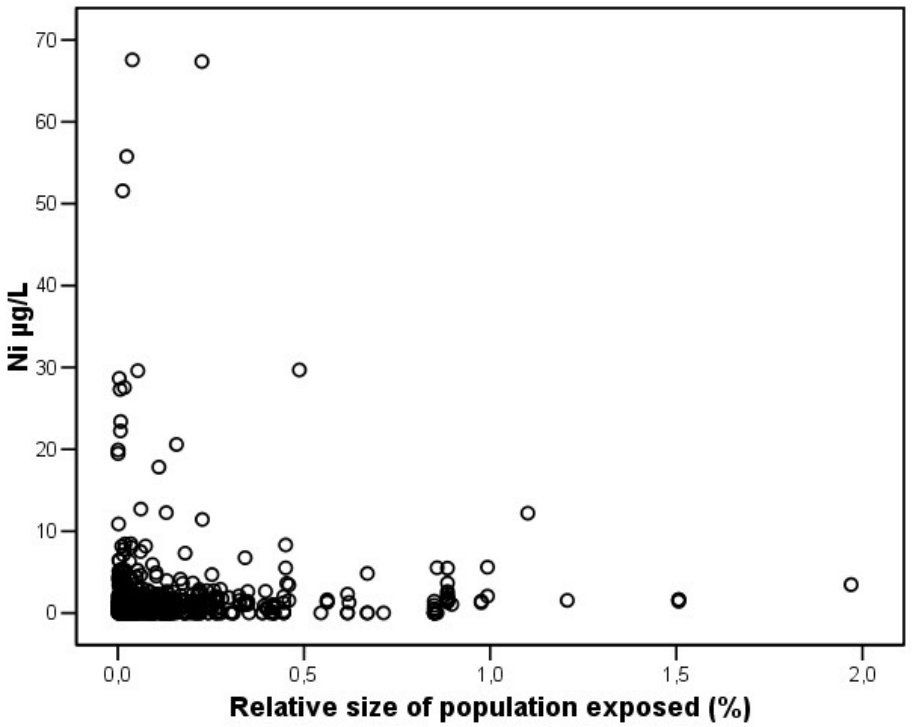


Figure 10: Ni concentration in 750 German tap water samples and % of the population exposed of the total population observed (n = 29,551,132).

A scattergram of Ni concentrations in tap water with the % of the population exposed of the total population observed (fig. 10) showed again a risk to a higher Ni exposure in smaller supply regions.

The Ni concentrations in the tap water samples showed a significant ($p < 0.05$) but only weak correlations to the Mo (0.255) and Zn (0.147) concentrations.

The regional distribution of Ni concentrations in German tap water are shown in fig. 21 in the annex to this work.

### 5.1.7 Lead

Tab. 27 displays the exposure of German population to Pb in tap water. Like Ni also Pb is considered as toxic element but again more than 98 % of all samples and more than 97 % of the population covered showed Pb concentrations below the maximum permissible value of 20 µg/L Pb according to the German drinking water ordinance (TrinkwV 2011), but more than 2 third of the samples representing more than half of the population observed are exposed to water with Pb concentrations below the lower limit of detection.

Table 27: Exposure of German population to Pb in tap water (% of samples of the entire number of samples taken (n = 750) and the % of the population exposed of the total population observed (n = 29,551,132))

| **Concentration of Pb (µg/L)** | **Percentage** | |
|---|---|---|
| | **of samples** | **of population exposed** |
| < LLD* | 63.3 | 55.6 |
| LLD – 2 | 27.7 | 35.9 |
| 2 – 5 | 5.90 | 3.49 |
| 5 – 10 | 1.90 | 2.00 |
| 10 – 20 ** | 1.10 | 2.61 |
| > 20 ** | 0.10 | 0.45 |

* LLD = Lower limit of detection
** Above maximum permissible value according to TrinkwV 2011)

However, with an average of 1.07 µg/L the Pb concentrations in German tap waters are well above the concentrations in mineral waters of German origin (0.69 µg/L Pb, tab. 9, chapter 3.5) indicating an anthropogenic influence on the Pb concentrations most likely from older plumbing materials. The strong anthropogenic background of the Pb in tap water might also explain why this element shows no correlation to any of the other elements in this study.

The well known anthropogenic origin of Pb in tap water explains also to a large extend the distribution of data in fig. 11, where the Pb concentration in tap water is plotted against the size of the supply units: severe enhanced Pb concentrations are more likely in smaller supply units.

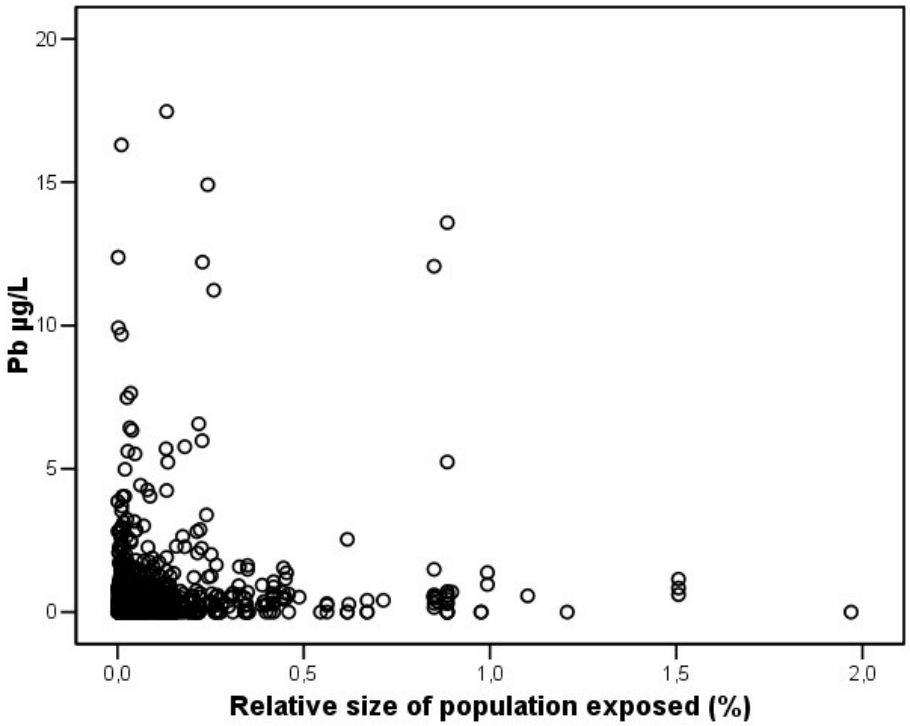


Figure 11: Pb concentration in 750 German tap water samples and % of the population exposed of the total population observed (n = 29,551,132).

The regional distribution of Pb concentrations in German tap water are shown in fig. 22 in the annex to this work.

### 5.1.8 Uranium

Tab. 28 displays the exposure of German population to U in tap water. Acknowledging the intensive and diverse discussion about permissible concentrations for U in drinking waters this table has a more detailed division of the concentration range. Until the end of the last century only a "guideline value" of 10 µg/L U was published by the WHO. Last but not least triggered to the ever increasing findings on U in mineral and tap waters (Sparovek et al. 2001,

Schnug et al. 2005, Knolle 2008) a controversial discussion left the public with consideration of the intensive and diverse discussion about permissible concentrations for U in drinking waters this table has a more detailed division of the concentration range. Tab. 28 shows that considering the larger data set with 4092 entries 3.3 % of all samples covering 1.31 % of the population observed are exposed to U concentrations above the anticipated critical value of 10 µg/L U (Vigelahn 2010). Considering the smaller data set with "only" 750 entries with 4.3 % number of samples with values above 10 µg/L U increases quite bit higher, but the percentage of the population exposed decreases slightly. Extreme exposure to concentrations above 20 µg/L U were observed in around 1 % of the samples covering less than 0.4 % of the population observed. In comparison UBA (2009) underestimates the figures for the number of cases with high U exposure to less than 0.6 % exposed to concentrations higher than 10 µg/L U and less than 0.1 % exposed to extreme concentrations above 20 µg/L U.

Table 28: Exposure of German population to U in tap water (% of samples taken and % of total population exposed)

| **Concentration of U (µg/L)** | **Percentage** | | | |
|---|---|---|---|---|
| | **of samples** | **of population exposed** | **of samples** | **of population exposed** |
| | n = 750 | n = 29,551,132 | n = 4092 | n = 60,354,408 |
| < LLD * | 25.2 | 31.9 | 3.70 | 11.7 |
| LLD – 0.2 | 19.1 | 20.6 | 20.5 | 27.1 |
| 0.2 – 2 | 31.7 | 37.4 | 58.2 | 49.4 |
| 2 – 5 | 10.0 | 5.29 | 10.1 | 7.64 |
| 5 – 10 | 9.60 | 4.58 | 4.20 | 2.85 |
| 10 – 15 ** | 2.80 | 0.24 | 1.80 | 0.71 |
| 15 – 20 ** | 0.50 | 0.02 | 0.60 | 0.22 |
| > 20 ** | 1.10 | 0.02 | 0.90 | 0.38 |

* LLD = Lower limit of detection
** above maximum permissible value according to TrinkwV 2011)

The map displayed in fig. 12 presents the regional distribution of the tap water samples (N = 4097) in Germany. The six different colours represent different U concentration ranges in µg/L (<0.5, 0.5-2, 2-5, 5-10, 10-20, >20) which reflect the different critical values for U in drinking water discussed since 2005 (BfR 2005: 0.2 µg/L U; WHO 1988, EFSA 2008: 2 µg/L U; UBA 2005: 10 µg/L U, action level by UBA 2010: 20 µg/L U).
U concentrations in waters show a distinctive regional distribution in Germany coming from the strong influence of the geological background. Information about the geological

background of this distribution were not task of this research work but can be found particularly for U in the work of Birke et al. (2008) and Knolle et al. (2008, 2011) .

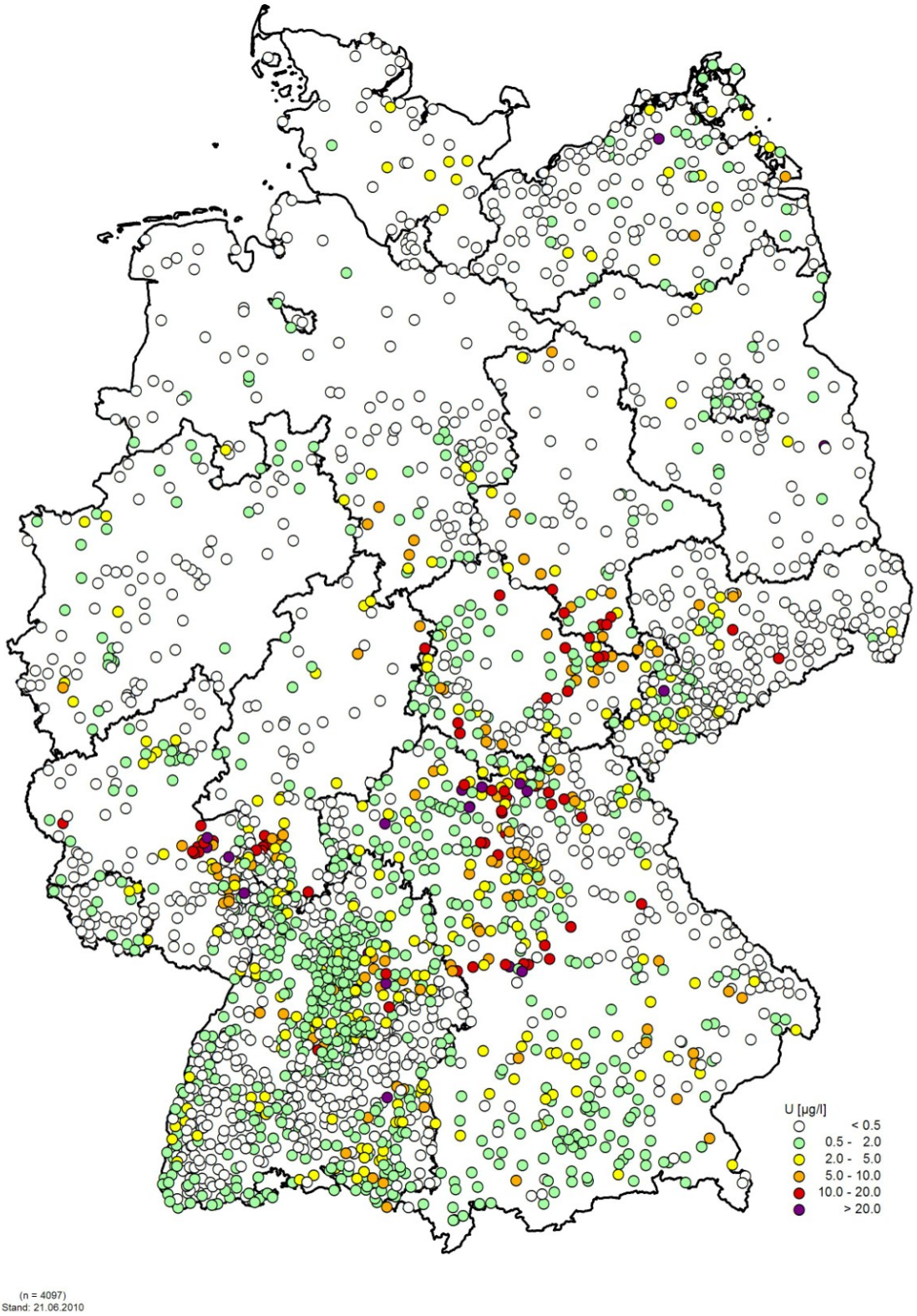


Figure 12: Regional distribution of U concentrations in German tap water(n = 4097)

The display of data in maps is one of the most successful methods to convey scientific information to the public. In a way maps can suggest illusions in the reader's mind, which are not supported by the data behind. A striking example is U in drinking water: figure 12 shows a number of "hotspots" in terms of U concentrations in tap waters across Germany, but indicates also that the majority of the samples contained low or only average amounts of U. The same information conferred in famous German a news journal looks much more dramatic (fig. 13).


Figure 13: Uranium contamination in German drinking water (from Schmundt 2010)

Tab. 29 presents a breakdown of the 4097 data sets for U by 16 individual federal counties and displays the percentage of the total population exposed to water with different U concentrations. The table allows also an evaluation to which extend the individual counties are represented in the entire survey. For all except two counties the population covered in % of the total population investigated reflects more or less the % of the counties entire population of the total German population of 80.6 million persons. Baden-Württemberg is with 21.4 % covered by the survey compared to a contribution of only 12.4 % to the German population overrepresented in comparison to North Rhine-Westphalia which is with only 16.6 % covered by the survey compared to a contribution of only 21.9 % to the German population underrepresented.

Table 29: U concentrations in tap water from German countries (Länder) sorted ascending with increasing population (pop.) access to waters with < 2µg/L U. (Citations for critical values: BfR 2005: 0.2 µg/L U; EFSA 2008, WHO 1988: 2 µg/L U; UBA 2005: 10 µg/L U, action level by UBA 2010: 20 µg/L U) sorted ascending with increasing population access to waters with < 2µg/L U

| | | | | | | | % of population covered | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **County** | **Area km²** | **Area %** | **Total population (* $10^6$)** | **% of total population** | **N of samples** | **Population covered in % of total population** | **< 0.2 µg/L U** | **0.2 - 2 µg/L U** | **2 - 5 µg/L U** | **5 - 10 µg/L U** | **10 - 20 µg/L U** |
| **Saxony-Anhalt** | 20.443 | 5.7 | 2.80 | 3.5 | 93 | 2.5 | 36.6 | 28.0 | 11.8 | 15.1 | 8.6 |
| **Thuringia** | 16.251 | 4.5 | 2.54 | 3.2 | 330 | 2.8 | 2.1 | 65.8 | 20 | 10.6 | 1.5 |
| **Hesse** | 21.114 | 5.9 | 5.90 | 7.3 | 126 | 5.3 | 23.8 | 44.4 | 17.5 | 7.1 | 7.1 |
| **Bavaria** | 70.553 | 19.7 | 11.60 | 14.4 | 630 | 11.7 | 21.1 | 49.4 | 14.5 | 7.6 | 5.7 |
| **Rhineland-Palatinate** | 19.486 | 5.4 | 3.88 | 4.8 | 298 | 4.6 | 34.9 | 39.6 | 9.7 | 5.0 | 7.4 |
| **Germany** | 358.921 | 100.0 | 80.61 | 100.0 | 4,095 | 100.0 | 22.3 | 59.0 | 10.9 | 4.5 | 2.5 |
| **Baden-Württemberg** | 35.751 | 10.0 | 10.00 | 12.4 | 1,333 | 21.4 | 8.5 | 75.4 | 11.2 | 3.0 | 1.2 |
| **Schleswig-Holstein** | 15.731 | 4.4 | 2.70 | 3.3 | 52 | 5.9 | 75.0 | 11.5 | 13.5 | 0.0 | 0.0 |
| **Saxony** | 18.338 | 5.1 | 4.60 | 5.7 | 344 | 6.0 | 62.5 | 26.5 | 7.6 | 1.7 | 1.5 |
| **Mecklenburg-Western Pomerania** | 23.170 | 6.5 | 1.85 | 2.3 | 485 | 2.9 | 1.7 | 89.5 | 5.4 | 2.3 | 0.6 |
| **Lower Saxony** | 47.343 | 13.2 | 7.48 | 9.3 | 150 | 6.8 | 62.0 | 29.3 | 6.0 | 2.7 | 0.0 |
| **North Rhine-Westphalia** | 37.070 | 10.3 | 17.69 | 21.9 | 109 | 16.6 | 45.0 | 48.6 | 5.5 | 0.9 | 0.0 |
| **Brandenburg** | 29.053 | 8.1 | 2.67 | 3.3 | 74 | 2.1 | 68.9 | 25.7 | 7,4 | 0.0 | 0.0 |
| **Saarland** | 2.570 | 0.7 | 1.08 | 1.3 | 38 | 1.5 | 43.6 | 51.3 | 5.1 | 0.0 | 0.0 |
| **Berlin** | 889 | 0.2 | 3.45 | 4.3 | 18 | 6.2 | 44.4 | 55.6 | 0.0 | 0.0 | 0.0 |
| **Bremen** | 404 | 0.1 | 0.68 | 0.8 | 6 | 0.9 | 50.0 | 50.0 | 0.0 | 0.0 | 0.0 |
| **Hamburg** | 755 | 0.2 | 1.69 | 2.1 | 8 | 2.9 | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 |

In contrast to the downscaling overall evaluation by UBA (Vigelahn et al. 2010) the exposure situation is quite different between the counties of Germany. This concerns especially the exposure to concentrations exceeding the anticipated critical value of 10 µg/L U and the extremes with more than 20 µg/L U. The largest population exposed to high U content in tap water and above the average for Germany (3.3 %) was found with 10.8 % in Rhineland-Palatinate followed by Saxony-Anhalt with 8.6 %, Bavaria with 7.4, Hesse with 7.1, the largest populations with an exposure below the lower limit of detection were found in Hamburg (100 %), Schleswig-Holstein (75 %) and Brandenburg (68.9 %). Except in the countries Lower Saxony, North Rhine-Westphalia, Brandenburg, Berlin, Bremen, Saarland and Hamburg samples with extreme U concentrations exceeding 20 µg/L were found, the largest number with 3.4 % of all samples in Rhineland-Palatinate, followed by Bavaria with 1.7 %, Baden-Württemberg with 0.7 %, Saxony with 0.2 and Hesse with 0.1 %. This are in total only 0.38 % of the entire population covered by this survey but this are in absolute figures 229,347 persons in the population observed, or if transposed to the entire German population 306,318 persons for which a higher health risk due to extreme U exposition can be assumed.

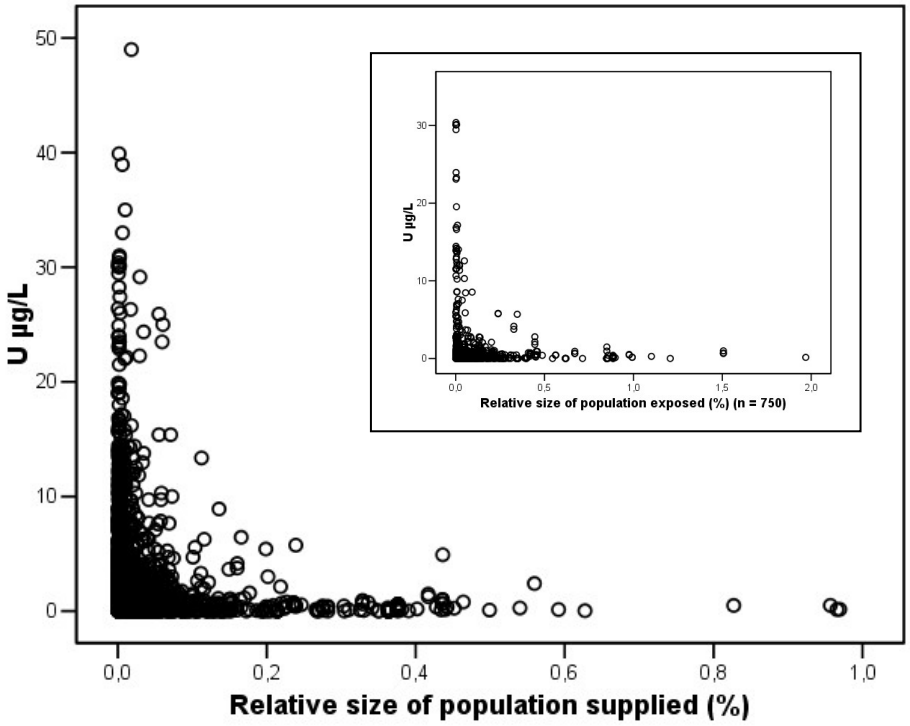


Figure 14: U concentration in 4095 German tap water samples and % of the population exposed of the total population observed (n = 60,354). Inlay graph: n = 750 and n = 29,551,132)

Fig. 14 shows the most expressed pattern for the relation between the size of the supply systems and the exposure to U in tap water. Again it shows that the risk of higher exposure to U in tap water is increasing with a decreasing size of a supply unit. A more detailed look into the frequency of the size of supply systems delivering water with more than 10 µg/L U in fig. 14 shows that such supply units serve usually a population of up to 5000 consumers, but high U concentrations may also occur in supply units serving more than 60.000 consumers. The use of shallow ground water for the supply of drinking water is common in small water supply systems, which are often located in rural areas. The distinct distribution pattern shown in fig. 14 gives further indications for the impact of fertiliser-derived U on ground and tap water (Smidt et al. 2011).

The U concentrations in the tap water samples showed a significant ($p < 0.05$) but only weak correlations to the B (0.110), Cu (-0.098) and Mo (0.138) concentrations.

### 5.1.9 Zinc

Tab. 30 displays the exposure of German population to Zn in tap water. The majority of three quarters of the samples and also of the population covered by this investigation showed exposure to Zn concentrations below 100 µ/g L which is only fraction of the concentration which is considered by WHO (2006) as "not acceptable to consumers". Only 1 % of the samples and much less than 1 % of the population covered by this investigation exceeded this value (tab. 30).

With an average of 151 µg/L the Zn concentrations in the tap waters were high above the concentration in mineral waters of German origin (0.73 µg/L Zn, Tab. 9, chapter 3.5) which underlines that anthropogenic sources contribute largely to the Zn concentrations in drinking water.

The value indicated by WHO (2006) is again far higher than the critical value for groundwater assigned by the German ordinance groundwater (58 µg/L Zn, GrwV 2010).

38.4 % of all samples representing a population covered of 35.9 % exceeded this value.

Like with B and Cu the reason for the remarkable difference between the critical values in both ordinances are that the higher one reflects on toxicological phenomena which may occur with the ingestion of waters with high Zn concentrations but the lower value for groundwater is meant as an indicator for anthropogenic influences (FAL 2007).

Table 30: Exposure of German population to Zn in tap water (% of samples of the entire number of samples taken (n = 458) and the % of the population exposed of the total population observed (n = 27,242,389))

| Concentration of Zn (µg/L) | Percentage | |
|---|---|---|
| | of samples | of population exposed |
| < LLD* | 2.80 | 2.64 |
| LLD – 100 | 73.4 | 74.8 |
| 100 – 200 | 8.70 | 7.33 |
| 200 – 500 | 8.70 | 4.97 |
| 500 – 3000 | 5.31 | 9.65 |
| > 3000** | 1.09 | 0.58 |

* LLD = Lower limit of detection
** Concentrations above "may not be acceptable to consumers" (WHO 2006), critical value for groundwater is 58 µg/L (GrwV 2010)

The high Zn concentrations in drinking water are most likely deriving from Zn containing plumbing materials and installations.

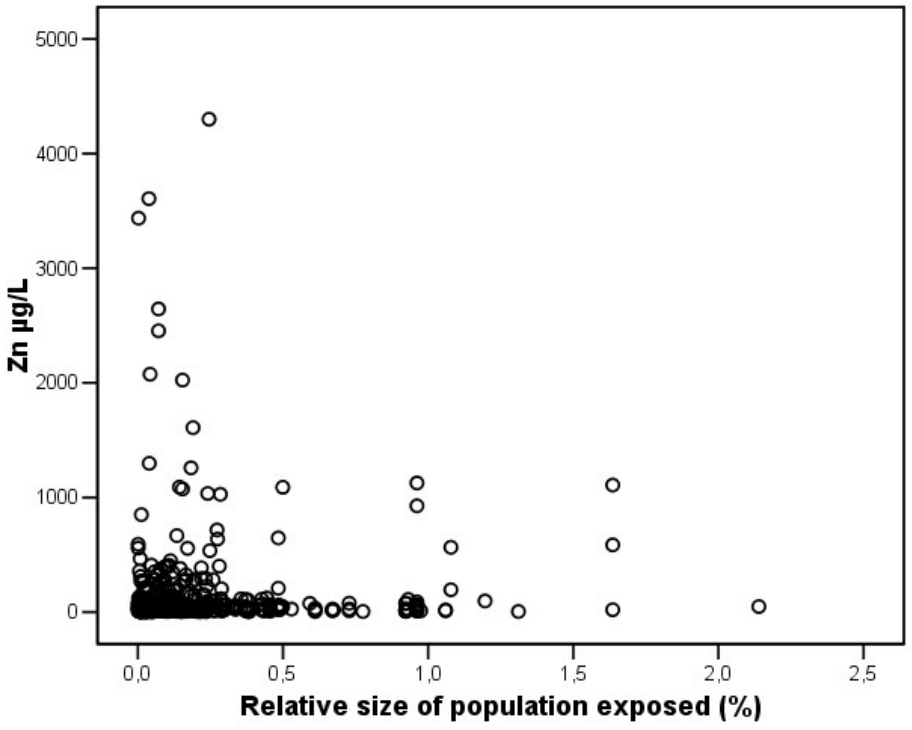


Figure 15: Zn concentration in 458 German tap water samples and % of the population exposed of the total population observed (n = 27,242,389)

The strong anthropogenic background might also be the reason for the although significant ($p < 0.05$) but very weak correlation of the Zn concentrations with only Mo (0.147) and Ni (0.459).

The scattergram of Zn concentration in tap water with the % of the population exposed of the total population observed (fig. 15) reveals again that consumers supplied with drinking water from smaller works are more likely to be exposed to higher Zn concentrations.

The regional distribution of Zn concentrations in German tap water are shown in fig. 23 in the annex to this work.

### 5.1.10 Population weighted mean concentrations for As, B, Cu, Li, Mo, Ni, Pb, U and Zn in German tap waters

In addition of the "percentage of population exposed" for mean and P 95 occurrence Tab. 31 shows the "population weighted mean", which is a new approach to assess exposure with elements in drinking water. The "population weighted mean" is the sum of all individual measurements multiplied with the "percentage of population covered" * 0.01. It is de facto the average concentration of As, B, Cu, Li, Mo, Ni, Pb, U or Zn to which the majority of the entire population covered is exposed. It is similar to the median value which is only the most frequently occurring value in a data set and therefore has only limited value for exposure estimates.

Table 31: Mean, population weighted mean (PWM) concentrations related population coverage (PC = and % of the population exposed of the total population observed) for As, B, Cu, Li, Mo, Ni, Pb, U and Zn in German tap waters

| Element | Median | | Mean | | PWM | | P95 | |
|---|---|---|---|---|---|---|---|---|
| | µg/L | % PC | µg/L | % PC | µg/L | % PC | µg/L | % PC |
| **As** | 0.661 | 56.6 | 0.63 | 56.6 | 1.27 | 89.2 | 3.21 | 98.7 |
| **B** | 21.0 | 37.2 | 43.1 | 54.1 | 40.7 | 57.9 | 102 | 89.8 |
| **Cu** | 19.5 | 40.8 | 105 | 75.4 | 78.8 | 65.4 | 356 | 90.7 |
| **Li** | 2.93 | 39.1 | 4.88 | 51.7 | 20.3 | 98.9 | 15.2 | 97.6 |
| **Mo** | 0.001 | 41.0 | 0.40 | 52.9 | 0.32 | 50.4 | 1.11 | 93.4 |
| **Ni** | 0.882 | 37.1 | 2.18 | 80.1 | 2.74 | 85.4 | 5.56 | 94.9 |
| **Pb** | 0.310 | 41.6 | 1.83 | 91.2 | 1.07 | 82.3 | 3.06 | 94.2 |
| **U*** | 0.280 | 57.8 | 0.51 | 70.9 | 1.45 | 92.8 | 8.00 | 99.6 |
| **U**** | 0.500 | 53.4 | 0.68 | 67.1 | 1.67 | 86.6 | 7.21 | 97.7 |
| **Zn** | 36.1 | 48.8 | 154 | 76.5 | 151 | 82.9 | 639 | 93.2 |

remarks: * n = 750 ; **n = 4095

In contrast the P 95 value gives the concentration which covers 95 % of all samples. Tab. 31 reveals that except for Cu, Mo and Ni the "population weighted mean" covers a larger percentage of the population with higher concentrations than the median or mean concentration value.

## 5.2 Individual diet exposure scenarios for As, B, Cu, Li, Mo, Ni, Pb, U and Zn

In the following chapter it will be investigated to which extend a change of dietary habits can affect an individual's daily intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn.

Tab. 32 shows for occurrence means and occurrence 95th percentile scenario the lowest intake scenario of the nine elements investigated in this study, tab. 33 the highest intake scenarios respectively.

Ovo-lacto vegetarian diets provide the lowest inputs of As, Cu, U and Zn with the solid diet, whereas carnivores have the lowest inputs with B, Li, Mo, Ni, and Pb (tab. 32). Looking at the complete input scenario which includes water ovo-lacto vegetarians drinking tap water stay lowest with As, and U, but staying low in Cu and Zn the ovo-lacto vegetarian would have to swap to German bottled waters or low mineralised waters from the world bottled water portfolio, because tap waters are notorious high contaminated with those elements from anthropogenic sources.

Table 32: Scenarios for lowest daily dietary intakes (solid + liquid) of As, B, Cu, Li, Mo, Ni, Pb, U and Zn at occurrence means and occurrence 95th percentile scenario

| | Lowest Intake Scenario | Daily intake of element (µg/day) | |
|---|---|---|---|
| | | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| As | Tap water consumer + Vegetarian (ovo-lacto) | 52.5 | 56.4 |
| B | Tap water consumer + Carnivore | 2,541 | 2,664 |
| Cu | German bottled water consumer + Vegetarian (ovo-lacto) | 2,345 | 2,361 |
| Li | Low mineralised bottled water consumer + Carnivore | 131 | |
| Mo | Tap water consumer + Carnivore | 426 | 427 |
| Ni | Tap water consumer + Carnivore | 274 | 279 |
| Pb | German bottled water consumer + Standard/ Carnivore | 112 | 115 |
| U | Tap water consumer + Vegetarian (ovo-lacto) | 4.36 | 17.5 |
| Zn | German bottled water consumer + Vegetarian (ovo-lacto) | 1,1302 | 1,1305 |

Carnivores keep low in B, Mo and Ni when staying with tap water, but for keeping a low Li and Pb input the liquids would have to come from German bottled waters.

Carnivore diets run high in As, Cu, U and Zn with their solids and with the exception of the well known anthropogenic influenced elements Cu, Pb and Zn which are provided excessively with tap waters rise to maximum levels when combined with high mineralised bottled waters (tab. 33).

Table 33: Scenarios for highest daily dietary intakes (solid + liquid) of As, B, Cu, Li, Mo, Ni, Pb, U and Zn at occurrence means and occurrence 95th percentile scenario

| | Highest Intake Scenario | Daily intake of element (µg/day) | |
|---|---|---|---|
| | | A: Occurrence means scenario | B: Occurrence 95th percentile scenario |
| As | High mineralised bottled water consumer + Carnivore | 972 | 1,235 |
| B | High mineralised bottled water consumer + Vegan | 11,018 | 26,802 |
| Cu | Tap water consumer + Carnivore | 6,548 | 7,101 |
| Li | High mineralised bottled water consumer + Vegan | 2,314 | 10,194 |
| Mo | High mineralised bottled water consumer + Vegan | 711 | 720 |
| Ni | High mineralised bottled water consumer + Vegan | 639 | 678 |
| Pb | Tap water consumer + Vegan | 204 | 208 |
| U | High mineralised bottled water consumer + Carnivore | 17.7 | 33.5 |
| Zn | Tap water consumer + Carnivore | 16,902 | 17,877 |

Among the nine elements investigated in this research work U shows the smallest range of variation in daily intake within the four dietary group types. An ovo-lacto vegetarian diet supplies the smallest amount of U with solid food to the human body (1.46 µg/day) whereas a carnivore diet delivers 1.4 times more U than an ovo-lacto vegetarian diet. The element U takes the seventh place among the nine elements in terms of the concentration range in drinking waters. A consumer of German tap or low mineralised bottled waters would have the lowest (2.9 µg/day), but a consumer of high mineralised bottled waters a 5.2 times higher intake of U (tab. 34).

Table 34: Mean values of As, B, Cu, Li, Mo, Ni, Pb, U and Zn intake estimates (µg/day) in different diet scenarios types and the contribution of waters to the daily intake of these elements (%) (dietary group types maintained at an energy input of 2000 kcal/day; water intake 2 L/day)

| **Intake (µg/day)** | **As** | **B** | **Cu** | **Li** | **Mo** | **Ni** | **Pb** | **U** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|
| **Reported *** | 142 | 1,650 | | | 220 | 213 | | 2.10 | 10,200 |
| **Standard diet**** (solid only) | 296 | 3,610 | 3,240 | 128 | 429 | 343 | 111 | 1.58 | 12,300 |
| **Standard diet + German tap water ***** | 299 | 3,691 | 3,398 | 169 | 430 | 349 | 113 | 4.48 | 12,602 |
| **Contribution of water at standard scenario (%)** | 1.00 | 2.20 | 4.65 | 24.3 | 0.23 | 1.72 | 1.77 | 64.7 | 2.40 |
| **High input scenario ******** | 1,235 HMBWC carnivore | 26,802 HMBWC vegan | 7,101 GTWC carnivore | 10,194 HMBWC vegan | 720 HMBWC vegan | 678 HMBWC vegan | 208 GTWC vegan | 33.5 HMBWC carnivore | 17,877 GTWC carnivore |
| **Contribution of water at high input scenario (%)** | 76.0 | 86.5 | 54.4 | 98.7 | 40.4 | 49.4 | 46.6 | 95.3 | 31.2 |
| **TDI*/*********** | 146 | - | 10,000 | 1,800 | - | 1,000 | 309 | 42 | - |
| **% of TDI at high input scenario** | 846 | - | 71.0 | 566 | - | 67.8 | 67.3 | 79.7 | - |
| **Recommended* or required (r/r)** | - | 1350 | 900 | 1,000 | 200 | 250 | - | - | 11,000 |
| **% of r/r at standard diet + German tap water scenario** | - | 273 | 378 | 16.9 | 215 | 140 | - | - | 115 |

Remarks: * Meta data analysis see tab. 8, chapter 3.4; ** see tab. 12-20, chapter 4; *** at occurrence means scenario; **** at occurrence 95th percentile scenario;
***** TDI: Tolerable Daily Intake for a 70 kg person; GTWC: German tap water consumer; HMBWC: High mineralised bottled water consumer

Except for Li, where in the standard scenario a quarter of the daily intake comes from tap water, the contribution of tap water to the total daily intake was always below 5 % (tab. 34).
These figures change dramatically when the scenario with the highest daily element intake is taken into account: for U and Li nearly the entire total daily intake (> 95 %) can be attributed to highly mineralised bottled water. In comparison, the corresponding values are for As and B >75 %, for Cu, Mo, Ni and Pb about 50 %, and for Zn 33 %. However, for the elements Cu, Pb and Zn (famously known for a strong anthropogenic background through plumbing materials) tap water is a more powerful contributor than even highly mineralised bottled waters (tab. 30). Consumers with a carnivore habit would take in more As, Cu, U and Zn, but vegans have a higher intake of B, Li, Mo, Ni and Pb with their solid food.

Compared to data reported in literature, standard conditions assumed in this work would deliver around twice as much daily intakes, except for Zn where the values from modelling met more or less the reported values. The largest discrepancy was with Li, where the reported values exceeded the modelled ones nearly four times (tab. 34).

At standard diet conditions (2000 kcal/day) and a daily consumption of 2 L, German tap water contributed in the model of this work 65 % of the total daily intake of U, 24 % of Li, 4.7 % of Cu, 2.4 % of Zn, 2.2 % of B, 1.8 % of Pb, 1.7 % of Ni, 1.00 % of As and 0.23 % of Mo respectively. High input scenarios for As and U occurred for high mineralised bottled water consuming carnivores, where the contribution of water to the daily intake reached 76.0 % and 95.3 % respectively. Consumption of high mineralised bottled water in combination with a vegan diet yielded the largest contribution of water to the daily diet for Li (98.7%) B (86.5), Ni (49.4 %), Mo (40.4 %). The largest contributions to the daily intake for Cu and Zn delivered a scenario of a German tap water consuming carnivore with 54.4 % and 31.2 %.

Compared with "tolerable daily intakes (TDI)" reported in the literature, in this study a German tap water consuming standard dieter would ingest already twice the TDI of As, but only between a tenth (U) and quarter (Pb) of the TDI for the other toxic elements (including Cu, Li, and Ni). Cu, Mo, Ni and Zn which are considered to be

essential for humans are sufficiently supplied in each of the diet/water scenarios. Except Li, which shows a very small bandwidth between toxic and beneficial action: the standard diet of a German tap water consumer would supply only 10 % of what is considered in literature to be beneficial, but the high input scenario of a high mineralised bottled water consuming vegan would exceed given TDI values by almost 6 times. A high mineralised bottled water consuming carnivore would take in nearly 9 times the TDI. For the other toxic elements (Cu, Ni, Pb, U) even at high input scenarios at maximum 70 % (Ni, Pb, Cu) to 80 % of the TDI (for U) were reached.

Table 35: Maximum reduction potential for daily dietary intakes (solid + liquid) of As, B, Cu, Li, Mo, Ni, Pb, U and Zn at means occurrence scenario

| | | | Maximum reduction potential at means occurrence scenario (%) |
|---|---|---|---|
| | High mineralised bottled water consumer + Carnivore | Tap water consumer + Vegetarian (ovo-lacto) | -94.6 |
| | High mineralised bottled water consumer + Vegan | Tap water consumer + Carnivore | -76.9 |
| | Tap water consumer + Carnivore | German bottled water consumer + Vegetarian (ovo-lacto) | -61.9 |
| | High mineralised bottled water consumer + Vegan | Low mineralised bottled water consumer + Carnivore | -94.3 |
| | High mineralised bottled water consumer + Vegan | Tap water consumer + Carnivore | -40.1 |
| | High mineralised bottled water consumer + Vegan | Tap water consumer + Carnivore | -57.0 |
| | Tap water consumer + Vegan | German bottled water consumer + Standard/ Carnivore | -33.1 |
| | High mineralised bottled water consumer + Carnivore | Tap water consumer + Vegetarian (ovo-lacto) | -75.4 |
| | Tap water consumer + Carnivore | German bottled water consumer + Vegetarian (ovo-lacto) | -22.1 |

Finally tab. 35 summarises the maximum reduction potential for daily dietary intakes (solid + liquid) of As, B, Cu, Li, Mo, Ni, Pb, U and Zn at means occurrence scenario. The greatest effect of changing an individual's dietary habits on the total daily element intake (considering the occurrence means scenario) would be expected with As and Li where the lowest intake scenario amounts to a nearly 95 % less intake than the highest one (tab. 35).

Also with U, relative to the maximum intake scenario the daily intake can be reduced to 75 % of this just by changing the dietary habits (tab. 35). With Zn the effects of changing ones dietary habits on the daily intake are lowest among the nine elements investigated in this study.

# 6 Conclusion

The main objective of the research work presented here was a statistical evaluation of the contribution of mineral and tap water to the dietary intake of As, B, Cu, Li, Mo, Ni, Pb, U and Zn by humans in order to identify potential hazards from contaminations with these elements through fertiliser use in agriculture.

Among the elements investigated in this study As and Li show the most susceptible bandwidth in daily intake through dietary habits: the highest input scenario for As (a highly mineralised bottled water consuming carnivore) supplies nearly 20 times more As than the lowest one (a German tap water consuming ovo-lacto vegetarian). In comparison, Zn is the element which daily intake varies only 1.5 times between lowest and highest input scenario. The ranking of the other elements from highest to lowest intake through dietary habits is As = Li > B > Cu = U = Ni > Pb > Mo > Zn. Among these elements U is the one with the highest contribution of waters to the dietary daily intake. Under standard diet conditions (see chapter 4) the contribution of German tap water to the daily intake decreased from 64.7 % for U over 24.3 for Li, to less than 5 % for Cu, Zn, B, Pb Ni and As (4.65 %, 2.40 %, 2.20 %, 1.77 %, 1.72 %, 1.00 %) to less than 1 % for Mo (0.23 %) (tab. 34, chapter 5).

According to the results of the research work presented here, changing the dieting habits at a whole can most affect the daily intake of As, where for instance a high mineralised bottled water consuming carnivore has a nearly 20 times higher daily dietary As intake compared to a tap water consuming ovo-lacto vegetarian. Similar high effects through changing the dietary habits are to expect with Li, but much smaller ones in the range of four times are to expect with B and U and a difference less than two times between highest and lowest intake scenario will occur for the elements Cu, Mo, Ni, Pb and Zn (tab. 32/33, chapter 5).
Within a particular diet the conscious selection of the drinking water is a much more comfortable strategy to influence the daily intake rather than to change the habits for selecting solid food. In case for the daily dietary As input it is obvious that it is much easier to convince an individual to change from using tap water instead of higher

contaminated high mineralised bottled waters than for a carnivore swapping stakes and sausages for veggies, and milk and egg products (tab. 35, chapter 5).

If in addition water is the main contributor to the daily dietary intake of a particular element, which is very much the case for the elements As, B, Li and U the selection of waters according to their element concentration would be another suitable avoidance strategy for increased intake.

Without further knowledge and for elements which are not strongly influenced by anthropogenic sources (like Cu, Pb and Zn) German tap waters are a perfect and preferable source for drinking waters especially when compared with high mineralised bottled waters.
However, in case of U some regions in Germany deliver waters with naturally high U concentrations (Smidt et al. 2011). Neither decocting nor filter equipment for household use is able to remove toxic elements and especially U from drinking water. For large scale application ion exchange systems are available, but they are expensive and produce follow up problems for a safe disposal because filters which after having accumulated U over time show increased radioactivity not only from U, but also from its much more hazardous decay product radon (Jekel et al. 2007). Despite this it makes not much sense to clean up tap water of which at maximum only 3 % is used for dietary purpose. 97 % of the tap water consumed by a private household ends up in bathroom sinks, toilets, dish washers and washing machines.

Much more efficient is to advise consumers replace the water needed for direct drinking and preparation for drinks and foods by bottled waters with a certified low U content. In this context the declaration of U in tap and mineral waters is a real showcase for efficient consumer protection just by giving relevant information: in regions with a high U load in tap waters they may swap their drinking water with bottled waters containing U below the detection limit, or check if their preferred bottled water could be replaced either by a one with lower U concentration or even tap water. For Germany this data are available online through Strahlentelex (Anonymous 2011).

Considering the significant amounts charged annually to agricultural land with mineral P fertilisers (see tab. 2, chapter 1) risks for "liquid entry" to the food chain for the elements investigated in this study arises primarily from U, which has a high mobility in soils and therefore is a serious contaminant or groundwater resources (Smidt et al. 2011). Recent research reveals that not only shallow groundwaters in the uppermost aquifers are at risk to fertiliser-derived U contaminations, but also deeper until now believed to be geologically protected and safe ground water bodies, preferably used for the production of bottled waters (Knolle et al. 2011).

Legislative bodies all over the world are very reluctant when it comes to reducing the environmental loads of heavy metals. If a hazardous substance has been identified as a treat for environmental and occupational health the first action taken by politicians is the hunt for a scapegoat on the input side or the general questioning of the health effects caused by a contaminant. Both are usually efficient measures to slow down or even prevent from any regulative processes. Exemplary for this are the elements As and especially Cd, where in case of Cd agriculture is responsible for approximately half of the environmental loads (UBA 2011). An exceptional didactic play in this context is U: although P-fertilisation in agriculture is the only relevant source for U loads (Kratz et al. 2011) neither Germany (Cordts 2011, Leiterer 2011) but also no other country in the world limits the U content in P fertilisers. This is more astonishing as the removal of U during the manufacturing process of P fertilisers is an old and well proven technology. When the U removed from P fertilisers also money is generated: not only in terms of the nuclear fuel itself, but also through a virtual reduction of atmospheric $CO_2$ loads. Schnug and Haneklaus (2011) estimated the overall benefits coming from U depleted P-fertilisers to around 1.8 €/kg P. In case of U, where agriculture is the only significant source of input to the environment and because recent research indicates leaching of U from arable soils and presence of fertiliser-derived U in ground and drinking water (Smidt et al. 2011), it is suggested that there should be a legit limitation in the fertiliser ordinance (Ekardt and Schnug 2008) as it would be the most promising measure to protect drinking water in Germany from further U contamination.

# 7 Abstract

Agriculture is a main contributor to environmental loads of nearly all elements of the periodic system. Not only waste-based fertiliser materials such as sewage sludge, but also mineral fertilisers, particularly mineral phosphorous fertilisers, contain significant amounts of elements which affect the quality of the environment and food plants. For the time period from 1950/51 to 2009/2010, the maximum annual loads of the elements As, Cd, Cu, Ni, Pb, Zn and U to agricultural land in Germany exclusively from the application of P fertilisers amounted to (T/a) As 73, Cd 42, Cu 146, Ni 91, Pb 11, U 228 and Zn 764 tons. Of this elements the quantitative whereabouts of Cd in the food chain is well investigated, but much less is known in this context for As, B, Cu, Li, Mo, Ni, Pb, U and Zn.

There are two major pathways through which elements enter the food chain: either by uptake of agricultural crops or by leaching into potable ground and surface water bodies. A closer look to the transfer pathways for such elements is of great importance when it comes to a risk assessment through which pathway elements that are applied together with fertilisation may enter the human body and which measures are suitable to influence the intake of these elements by humans, either with view to the prevention of intake negatively affecting health, or with the objective to compensate deficiency of an essential micro nutrient.

Finally, for a correct assessment of risks arising from a dispersal of these elements with fertilisers in the environment it is necessary to know to which extent each of the two general pathways, solid or liquid food, contributes to their total daily intake. This information is particularly required in order to assess efficient abatement strategies for contaminations in the food chain.

Methodically the research work uses meta data analysis for element concentration of solid foods and real analytical data for element concentrations in tap and mineral waters. Element loads were calculated for the waters on basis of a consumption of 2 L/day. To estimate the loads through solid foods in this study a standardised healthy diet has been designed based on an energy requirement of 2000 kcal/day and according to the rules of the known “nutrition pyramid".

The standard diet has been diversified in three additional diet types: an ovo-lacto vegetarian, a vegan and a carnivore type, but always maintained at an energy input of 2000 kcal/day.

Compared to data reported in literature, standard conditions assumed in this work would deliver around twice as much daily intakes, except for Zn where he values from modeling met more or less the reported values. The largest discrepancy was with Li, where the reported values exceeded the modeled ones nearly four times.

At standard diet conditions (2000 kcal/day) and a daily consumption of 2 L, German tap water contributed in the model of this work 65 % of the total daily intake of U, 24 % of Li, 4.7 % of Cu, 2.4 % of Zn, 2.2 % of B, 1.8 % of Pb, 1.7 % of Ni, 1.00 % of As and 0.23 % of Mo respectively. High input scenarios for As and U occurred for high mineralised bottled water consuming carnivores, where the contribution of water to the daily intake reached 76.0 % and 95.3 % respectively. Consumption of high mineralised bottled water in combination with a vegan diet yielded the largest contribution of water to the daily diet for Li (98.7 %) B (86.5), Ni (49.4 %), Mo (40.4 %). The largest contributions to the daily intake for Cu and Zn delivered a scenario of a German tap water consuming carnivore with 54.4 % and 31.2 %.

Compared with "tolerable daily intakes (TDI)" reported in the literature, in this study a German tap water consuming standard dieter would ingest already twice the TDI of As, but only between a tenth (U) and a quarter (Pb) of the TDI for the other toxic elements (including Cu, Li and Ni). Cu, Mo, Ni and Zn which are considered to be essential for humans are sufficiently supplied in each of the diet/water scenarios. Except Li, which shows a very small bandwidth between toxic and beneficial action: the standard diet of a German tap water consumer would supply only 10 % of what´s considered in literature to be beneficial, but the high input scenario of a high mineralised bottled water consuming vegan would exceed given TDI values by almost 6 times. A high mineralised bottled water consuming carnivore would take in nearly 9 times the TDI. For the other toxic elements (Cu, Ni, Pb, U) even at high input scenarios at maximum 70 % (Ni, Pb, Cu) to 80 % of the TDI (for U) were reached.

This study shows that drinking water is a prime source for the dietary intake of As, B, Cu, Li, Mo, Ni, Pb and Zn only when high mineralised bottled waters are used. If the daily requirements for water are satisfied with German tap waters, the contribution of drinking water to the daily intake does not exceed 5 %. The clear exception is U, where already under standard diet conditions on an average more than 2 third of the daily U intake comes from waters. Fortunately information on the U concentrations in tap water and bottled waters are available and enable the consumer to choice sources with low or nearly zero U concentration for minimising personal health risks.

Although a ubiquitous natural occurring radionuclide, significant amounts of U are brought into soils and waters through the use of mineral P fertilisers in agriculture. Because fertilisation is the only significant source for anthropogenic U contaminations in the environment politicians are well advised to regulate this loads through fertiliser laws in order to protect the quality of drinking water for future generations for the sake of sustainability.

**Zusammenfassung: Beitrag von Mineral- und Leitungswässern zur Aufnahme von As, B, Cu, Li, Mo, Ni, Pb, U und Zn mit der menschlichen Nahrung**

Durch landwirtschaftliche Aktivitäten werden insbesondere über die Düngung fast alle Elemente des Periodensystems in Agrarökosysteme eingetragen. Dabei sind die Quellen dieser Stoffeinträge nicht nur aus Abfällen und Reststoffen gewonnene Düngemittel, sondern in ganz besonderem Maße auch mineralische Phosphor Dünger. Im Zeitraum von 1950/51 bis 2009/2010 betrugen die maximalen jährlichen Einträge an Cd, Cu, Ni, Pb, Zn und U in landwirtschaftlich genutzte Böden Deutschlands allein über P-haltige Handelsdünger: As 73, Cd 42, Cu 146, Ni 91, Pb 11, U 228 und Zn 764 Tonnen. Der quantitative Verbleib des Elementes Cd im Agrarökosystem und der Nahrungskette ist dabei vergleichsweise gut erforscht, relativ wenig bekannt ist in diesem Kontext jedoch von den Elementen B, Cu, Li, Mo, Ni, Pb, U und Zn. Sie gelangen entweder über die Aufnahme landwirtschaftlicher Kulturpflanzen oder nach Auswaschung aus dem Boden ins Grundwasser über das Trinkwasser in die Nahrungskette. Der Anteil beider Pfade an der Gesamtaufnahme ist dabei elementspezifisch. Je nachdem, welcher dieser beiden Pfade dominiert sind Maßnahmen zur Minderung des Eintrages toxischer Elemente wie zu U oder ggf. auch der Erhöhung der täglichen Zufuhr mit der Nahrung bei essentiellen (z.B. Cu und Zn) oder nützlichen Elementen (z.B. Li) zu gestalten.
Methodisch wurden die Elementkonzentrationen in festen Nahrungsmitteln über eine Metadatenanalyse, diejenigen in Mineral- und Leitungswässern durch Analyse realer Proben bestimmt. Elementfrachten wurden auf Basis eines täglichen Flüssigkeitskonsums von 2 L berechnet.
Zur Berechnung der täglichen Elementzufuhren über feste Nahrung wurde eine gesunde und ausgewogene Standardernährung auf Basis von 2000 kcal/d und einer

Verteilung der Nahrungsmittelgruppen entsprechend der „Nahrungspyramide“ konzipiert. Aus dieser Standardernährung wurden drei weitere extreme Ernährungspläne abgeleitet und zwar der eines ovo-lactobilen Vegetariers, eines Veganers und eines Fleischkonsumenten, die aber ebenfalls stets auf eine tägliche Energiezufuhr von 2000 kcal abgestimmt waren. Im Vergleich zu in der Literatur berichteten täglichen Elementaufnahmen lagen, mit Ausnahme von Zn, diejenigen der Modellszenarien dieser Arbeit etwa doppelt so hoch. Unter Standardbedingungen (Standadernährungsplan, 2000 kcal/d, 2 L Flüssigkeitsaufnahme) betrug der Beitrag deutschen Leitungswassers zur Gesamtelementaufnahme bei U 65 %, Li 24 %, Cu 4,7 %; Zn 2,4 %; B 2,2 %; Pb 1,8 %; Ni 1,7 %; As 1,00 % und Mo nur noch 0,23 %. Besonders hohe tägliche Zufuhren ergaben sich für As und U bei einem hoch mineralisierte Flaschenwässer trinkenden Fleischkonsumenten. Der Anteil des Trinkwassers an der täglichen Gesamtaufnahme erreicht dabei bis zu 76,0 % bei As und 95,3 % bei U. Bei Veganern, die hoch mineralisierte Flaschenwässer konsumieren, lag der Beitrag des Wassers an der täglichen Elementzufuhr für Li bei 98,7 %, für B bei 86,5 %, für Ni bei 49,4 % und für Mo bei 40,4 %. Den größten Beitrag von Flüssigkeiten an der täglichen Cu- und Zn- Zufuhr haben deutsches Leitungswasser trinkenden Fleischkonsument, und zwar mit 54,4 % bzw 31,2 %.
Verglichen mit in der Literatur veröffentlichten TDI-Werten "Tolerable Daily Intakes” würde nach den Ergebnissen dieser Studie ein sich normal ernährender Konsument deutschen Leitungswassers bereits die doppelte Menge an As, aber nur zwischen einem Zehntel (U) und einem Viertel (Pb) des TDI der anderen untersuchten toxischen Elemente (einschließlich Cu, Li und Ni) aufnehmen. Die ebenfalls essentiellen Elemente Cu, Mo, Ni und Zn wurden in jedem der Ernährungsszenarios dieser Arbeit in ausreichenden Mengen zugeführt. Eine Ausnahme ist Li, wo die Bandbreite zwischen nützlicher und toxischer Wirkung ausgesprochen schmal ist: ein sich normal ernährender Konsument deutschen Leitungswassers nimmt täglich lediglich 10 % der als optimal angesehenen Menge an Li auf, bei einem hoch mineralisierte Flaschenwässer konsumierenden Veganer hingegen überschreitet die tägliche Li-Aufnahme den TDI Wert um das Sechsfache, bei einem entsprechenden Fleischkonsumenten um das Neunfache. Für die anderen in dieser Arbeit untersuchten toxischen Elemente (Cu, Ni, Pb, U) wurden selbst bei den Szenarien mit höchster täglicher Zufuhr maximal 70 % (Ni, Pb, Cu) bis 80 % (U) des TDI erreicht.

Die Ergebnisse dieser Arbeit zeigen, dass Trinkwasser nur dann eine signifikante Quelle für die tägliche Aufnahme an As, B, Cu, Li, Mo, Ni, Pb und Zn ist, wenn hochmineralisierte Flaschenwässer konsumiert werden. Bei ausschließlichem Genuss deutschen Leitungswassers übersteigt der Beitrag der täglichen Zufuhr mit Flüssigkeit keine 5 %.

Eindeutige Ausnahme ist jedoch U, wo bereits unter den Bedingungen einer Standardernährung zwei Drittel der täglichen U-Aufnahme über das Wasser erfolgt. Die tägliche Zufuhr kann jedoch durch bewussten Konsum drastisch minimiert werden, indem bei der Wahl des Trinkwassers die Option mit der jeweils geringsten U-Konzentration gewählt wird.

Obgleich U ein allgegenwärtiges natürliches toxisches und radioaktives Schwermetall ist, werden durch den Einsatz mineralischer P-Dünger in der Pflanzenproduktion Trinkwasservorräte zusätzlicher, durch geeignete ordnungspolitische Maßnahmen im Bereich des Düngemittelrechtes jedoch einfach vermeidbarer Belastungen ausgesetzt.

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# 9 Annex

Table 36 annex: Estimated mean soil-to-plant transfer of selected minerals

| Element | Plant | Factor | Reference |
|---|---|---|---|
| As | General 0.04 | TF | Baes et al. (1984) |
| | Rice, grain 0.068-0.44 | CF | Huang et al. (2006) |
| | Grass 0.01 | BC | Overesch et al (2007) |
| | Vegetable: $3.2x10^{-4}$ | BC | Environm. Agency (2009) |
| | Cabbage $10.9x10^{-4}$ | BC | Uchida et al. (2007) |
| | Spinach $5.3x10^{-3}$ | BC | Uchida et al. (2007) |
| | Potato $11.3x10^{-4}$ | BC | Uchida et al. (2007) |
| | Wheat $5.2x10^{-4}$ | BC | Uchida et al. (2007) |
| B | Mean 4.0 | TF | Baes et al. (1984) |
| Cu | General 0.40 | TF | Baes et al. (1984) |
| | Gras: 0.16 (CF 20.1) | BC | Overesch et al. (2007) |
| | Cabbage $6.02x10^{-2}$ | BC | Uchida et al. (2007) |
| | Spinach $3.9x10^{-2}$ | BC | Uchida et al. (2007) |
| | Potato $1.6x10^{-1}$ | BC | Uchida et al. (2007) |
| | Wheat $1.1x10^{-1}$ | BC | Uchida et al. (2007) |
| Li | General 0.025 | TF | Baes et al. (1984) |
| | Cabbage $15.5x10^{-4}$ | BC | Uchida et al. (2007) |
| | Spinach $3.2x10^{-3}$ | BC | Uchida et al. (2007) |
| | Potato $6.8x10^{-4}$ | BC | Uchida et al. (2007) |
| | Wheat $10.1x10^{-5}$ | BC | Uchida et al. (2007) |
| Mo | General 0.25 | TF | Baes et al. (1984) |
| | Cabbage $9.5x10^{-1}$ | BC | Uchida et al. (2007) |
| | Spinach $3.4x10^{-1}$ | BC | Uchida et al. (2007) |
| | Potato $1.8x10^{-1}$ | BC | Uchida et al. (2007) |
| | Wheat $3.3x10^{-1}$ | BC | Uchida et al. (2007) |
| Ni | General 0.060 | TF | Baes et al. (1984) |
| | Wheat 0.12-0.75 | BC | NUREG (2003) |
| | Soybean 0.022->1.1 | BC | NUREG (2003) |
| | Gras 0.45 (CF 45.8) | BC | Overesch et al. (2007) |
| Pb | General 0.045 | TF | Baes et al. (1984) |
| U | General $8.5x10^{-3}$ | TF | Baes et al. (1984) |
| | Cabbage $23.9x10^{-5}$ | BC | Uchida et al. (2007) |
| | Spinach $2.7x10^{-3}$ | BC | Uchida et al. (2007) |
| | Potato $9.5x10^{-4}$ | BC | Uchida et al. (2007) |
| | Wheat $11.0x10^{-5}$ | BC | Uchida et al. (2007) |
| Zn | General 1.5 | TF | Baes et al. (1984) |
| | Gras 0.21 (CF 23.7) | BC | Overesch et al. (2007) |

TF – transfer factor; BC - bioaccumulation coefficients = $X_{plant} / X_{soil\ (total)}$ ;CF – Concentration factor = $X_{plant} / X_{soil\ (available)}$

Table 37 annex: Descriptive statistics of As concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 23 | 0.093 | 0.05 | 0.006 | 0.303 | 0.009 | Roychowdhury et al. 2002, Schoof et al. 1999, Del Razo et al. 2002, Muñoz et al. 2005, Prasad 2008, Delgado-Andrade 2003, SCOOP 2004, Bednarek et al. 2006, Ysart et al. 1999, Leblance et al. 2005, Abernathy 2001, McLaughlin et al. 1999, Simsek et al. 2000, FSA 2006, Brown and Balls 1997, Pinkney 2003, JECFA 1983, FSA 1998, López-Alonsoet al. 2007, Gorbunov et al. 2004, ATSDR 2007, Reilly 2002 |
| Vegetables | 25 | 0.044 | 0.02 | 0.003 | 0.322 | 0.004 | |
| Milk and milk products | 28 | 0.01 | 0.004 | 0.0002 | 0.062 | 0.009 | |
| Eggs | 11 | 0.009 | 0.006 | 0.001 | 0.026 | 0.009 | |
| Fruits | 14 | 0.009 | 0.007 | 0.001 | 0.024 | 0.007 | |
| Meat and meat products | 19 | 0.022 | 0.02 | 0.003 | 0.102 | 0.001 | |
| Offal | 13 | 0.013 | 0.012 | 0.003 | 0.033 | 0.006 | |
| Fish and fish products | 25 | 2.26 | 1.66 | 0.016 | 6.23 | 3.67 | |
| Shellfish | 21 | 5.91 | 2.94 | 0.008 | 32.9 | 53.1 | |

Table 38 annex: Descriptive statistics of B concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 26 | 2.5 | 1.69 | 0.104 | 18.0 | 12.5 | Nielsen 1997, Green Facts 2004, Richold 1998, Choi and Jun 2008, MPCA 1998, ATSDR 2010, Ysart et al. 1999, Pinkney 2003, FSA 1998, EGVM 2002, Souci et al. 2000, Simsek et al. 2003, Hunt et al. 1991, Reilly 2002, EPA 2008 |
| Vegetables | 30 | 4.14 | 2.39 | 0.793 | 30.0 | 30.5 | |
| Milk and milk products | 20 | 0.542 | 0.35 | 0.014 | 1.97 | 0.266 | |
| Eggs | 12 | 0.235 | 0.234 | 0.014 | 0.56 | 0.036 | |
| Fruits | 31 | 5.95 | 5.25 | 1.35 | 30.0 | 29.4 | |
| Meat and meat products | 20 | 0.291 | 0.307 | 0.015 | 0.74 | 0.042 | |
| Offal | 10 | 0.467 | 0.395 | 0.069 | 0.979 | 0.098 | |
| Fish and fish products | 12 | 0.431 | 0.45 | 0.1 | 0.95 | 0.074 | |
| Shellfish | 10 | 1.7 | 1.46 | 0.94 | 2.78 | 0.351 | |

Table 39 annex: Descriptive statistics of Cu concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 20 | 1.92 | 1.63 | 0.64 | 4.58 | 1.08 | Onianwa et al. 2001, Iyaka 2007, Massányi et al. 2001, Obasohan 2007, Gerber et al. 2008, Demirezen and Uruc 2006, Bednarek et al. 2006, Tripathi et al. 1997, Ysart et al. 1999, Prasad 2008, Leblance et al. 2005, Simsek et al. 2000, Olivares et al. 2004, Ashraf 2006, FSA 2006, Radwan and Salama 2006, HC 1993-1999, HC 2000, HC 2001, HC 2002, Fakayode and Olu-Owolabi 2003, Brown and Balls 1997, Pinkney 2003, Schroeder 1971, FSA 1998, López-Alonsoet al. 2007, Kirkpatrick and Coffin 1975, Souci et al. 2000, Santos et al. 2004, Hunt et al. 1991, ATSDR 2004, Reilly 2002, Somer and Unal 2004, De pieri et al. 1996 |
| Vegetables | 31 | 1.88 | 1.68 | 0.598 | 5.5 | 1.66 | |
| Milk and milk products | 20 | 0.487 | 0.322 | 0.05 | 1.91 | 0.278 | |
| Eggs | 15 | 0.962 | 0.75 | 0.5 | 4.1 | 0.777 | |
| Fruits | 20 | 2.07 | 1.51 | 0.358 | 7.82 | 3.04 | |
| Meat and meat products | 22 | 1.78 | 1.23 | 0.086 | 6.8 | 2.36 | |
| Offal | 20 | 35.7 | 20.8 | 6.19 | 149 | 1211 | |
| Fish and fish products | 25 | 0.782 | 0.425 | 0.077 | 4.74 | 0.919 | |
| Shellfish | 25 | 10.5 | 5.4 | 1.49 | 67.0 | 260 | |

Table 40 annex: Descriptive statistics of Li concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 7 | 0.208 | 0.02 | 0.015 | 0.798 | 0.099 | Ysart et al. 1999, Leblance et al. 2005, FSA 1998,Schrauzer. 2002, Evans and Read 1985 |
| Vegetables | 7 | 0.159 | 0.015 | 0.01 | 0.685 | 0.071 | |
| Milk and milk products | 6 | 0.094 | 0.012 | 0.003 | 0.5 | 0.04 | |
| Eggs | 2 | 0.011 | 0.011 | 0.007 | 0.014 | 0.04 | |
| Fruits | 5 | 0.025 | 0.008 | 0.005 | 0.09 | 0.001 | |
| Meat and meat products | 5 | 0.009 | 0.01 | 0.004 | 0.013 | 0.003 | |
| Offal | 2 | 0.036 | 0.036 | 0.03 | 0.041 | 0.002 | |
| Fish and fish products | 4 | 0.033 | 0.028 | 0.017 | 0.06 | 0.003 | |
| Shellfish | 6 | 0.155 | 0.126 | 0.074 | 0.337 | 0.009 | |

Table 41 annex: Descriptive statistics of Mo concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 16 | 0.41 | 0.33 | 0.186 | 0.967 | 0.048 | Rajagopalan 1988, Prasad 2008 Tsongas et al. 1980, Gerber et al. 2008, Ysart et al. 1999, Leblance et al. 2005, HC 1993-1999, Pinkney 2003, Schroeder 1971, FSA 1998, López-Alonsoet al. 2007, Souci et al. 2000, Hunt et al. 1991, Reilly 2002, Somer and Unal 2004, Ensafi and Khaloo 2005, Gao and Siow 1996, De pieri et al. 1996 |
| Vegetables | 23 | 0.639 | 0.486 | 0.049 | 2.42 | 0.383 | |
| Milk and milk products | 17 | 0.096 | 0.084 | 0.025 | 0.18 | 0.003 | |
| Eggs | 11 | 0.195 | 0.12 | 0.067 | 0.49 | 0.026 | |
| Fruits | 17 | 0.208 | 0.154 | 0.01 | 0.656 | 0.039 | |
| Meat and meat products | 14 | 0.114 | 0.088 | 0.021 | 0.36 | 0.010 | |
| Offal | 8 | 1.156 | 1.11 | 0.683 | 1.97 | 0.201 | |
| Fish and fish products | 13 | 0.138 | 0.065 | 0.003 | 0.385 | 0.021 | |
| Shellfish | 12 | 0.438 | 0.337 | 0.01 | 1.25 | 0.157 | |

Table 42 annex: Descriptive statistics of Ni concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 27 | 0.375 | 0.312 | 0.044 | 0.995 | 0.071 | Flyvholm et al. 1984, Onianwa et al. 2000, Erdoğrul and Erbilir 2006, Massányi et al. 2001, Obasohan 2007, Demirezen and Uruc 2006, Bednarek et al. 2006, Ysart et al. 1999, Leblance et al. 2005, Ashraf 2006, Prasad 2008, FSA 2006, Tsoumbaris and Tsoukali-Papadopoulou 1994, HC 2000, HC 2001, HC 2002, Fakayode and Olu-Owolabi 2003, Pinkney 2003, FSA 1998, López-Alonsoet al. 2007, Kirkpatrick and Coffin 1975, Souci et al. 2000, Ellen et al. 1978, Santos et al. 2004, Thomas et al. 1974, ATSDR 2005, Reilly 2002 |
| Vegetables | 27 | 0.294 | 0.203 | 0.084 | 0.84 | 0.05 | |
| Milk and milk products | 19 | 0.055 | 0.039 | 0.007 | 0.16 | 0.002 | |
| Eggs | 15 | 0.043 | 0.03 | 0.006 | 0.168 | 0.002 | |
| Fruits | 24 | 0.45 | 0.22 | 0.026 | 1.82 | 0.303 | |
| Meat and meat products | 26 | 0.165 | 0.078 | 0.011 | 0.823 | 0.035 | |
| Offal | 13 | 0.093 | 0.065 | 0.017 | 0.37 | 0.009 | |
| Fish and fish products | 24 | 0.234 | 0.113 | 0.02 | 1.21 | 0.08 | |
| Shellfish | 11 | 0.203 | 0.123 | 0.02 | 0.61 | 0.038 | |

Table 43 annex: Descriptive statistics of Pb concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 40 | 0.065 | 0.027 | 0.002 | 0.7 | 0.014 | Forte and Bocca 2007, Karavoltsos et al. 2008, Erdoğrul and Erbilir 2006, Muñoz et al. 2005, Massányi et al. 2001, SCOOP 2004, Obasohan 2007, Gerber et al. 2008, Demirezen and Uruc 2006, Bednarek et al. 2006, Tripathi et al. 1997, Sapunar-Postruznik et al. 1996, Ysart et al. 1999, Leblance et al. 2005, McLaughlin et al. 1999, Simsek et al. 2000, Ashraf 2006, FSA 2006, Tsoumbaris and Tsoukali-Papadopoulou 1994, Radwan and Salama 2006, HC 1993-1999, HC 2000, HC 2001, HC 2002, Fakayode and Olu-Owolabi 2003, Brown and Balls 1997, Pinkney 2003, FSA 1998, López-Alonsoet al. 2007, Gorbunov et al. 2004, Santos et al. 2004, ATSDR 2007, Reilly 2002, Somer and Unal 2004, Prasad 2008 |
| Vegetables | 44 | 0.178 | 0.04 | 0.002 | 1.83 | 0.109 | |
| Milk and milk products | 31 | 0.022 | 0.015 | 0.001 | 0.122 | 0.001 | |
| Eggs | 21 | 0.037 | 0.006 | 0.001 | 0.59 | 0.016 | |
| Fruits | 27 | 0.091 | 0.027 | 0.003 | 0.64 | 0.023 | |
| Meat and meat products | 35 | 0.067 | 0.02 | 0.003 | 0.687 | 0.016 | |
| Offal | 37 | 0.146 | 0.067 | 0.005 | 0.752 | 0.033 | |
| Fish and fish products | 33 | 0.064 | 0.02 | 0.0003 | 0.4 | 0.011 | |
| Shellfish | 21 | 0.208 | 0.099 | 0.002 | 0.75 | 0.07 | |

Table 44 annex: Descriptive statistics of U concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 15 | 0.001975 | 0.00204 | 0.000248 | 0.00343 | > 0.00001 | Galletti et al. 2003, HC 2000, HC 2001, HC 2002, Schnug et al. 2005, Bernhard 2005, Prasad 2008, Santos et al. 2004, Amaral et al. 2005, Garcia et al. 2006, Efsa 2009, Dang et al. 1990, Prasad 2008, Chung et al. 2000, Akhter et al. 2003, ATSDR 1999, FSA 2004, Tracy et al. 1983, Kumar et al. 2009 |
| Vegetables | 16 | 0.0013216 | 0.0011955 | 0.0002 | 0.00325 | > 0.00001 | |
| Milk and milk products | 22 | 0.00069605 | 0.000268 | 0.00005 | 0.004 | > 0.00001 | |
| Eggs | 12 | 0.000221 | 0.00019 | 0.00005 | 0.0006 | > 0.00001 | |
| Fruits | 16 | 0.0005956 | 0.0003525 | 0.00004 | 0.00236 | > 0.00001 | |
| Meat and meat products | 23 | 0.00117448 | 0.000378 | 0.00007 | 0.0095 | > 0.00001 | |
| Offal | 7 | 0.001389 | 0.0012 | 0.00033 | 0.0035 | > 0.00001 | |
| Fish and fish products | 18 | 0.0017646 | 0.001173 | 0.000001 | 0.0065 | > 0.00001 | |
| Shellfish | 5 | 0.008416 | 0.00673 | 0.0029 | 0.02025 | > 0.00001 | |

Table 45 annex: Descriptive statistics of Zn concentrations in solid foods mg/kg

| | N | Mean | Median | Minimum | Maximum | Variance | References |
|---|---|---|---|---|---|---|---|
| Cereal and cereal products | 28 | 15.5 | 10.1 | 5.5 | 32.7 | 86.2 | Scherz and Kirchhoff 2006, Onianwa et al. 2001, Iyaka 2007, Prasad 2008, Massányi et al. 2001, Obasohan 2007, Gerber et al. 2008, Demirezen and Uruc 2006, Bednarek et al. 2006, Tripathi et al. 1997, Ysart et al. 1999, Leblance et al. 2005, Simsek et al. 2000, Olivares et al. 2004, FSA 2006, Tsoumbaris and Tsoukali-Papadopoulou 1994, Radwan and Salama 2006, HC 1993-1999, HC 2000, HC 2001, HC 2002, Fakayode and Olu-Owolabi 2003, Brown and Balls 1997, Pinkney 2003, Schroeder 1971, FSA 1998, López-Alonsoet al. 2007, Kirkpatrick and Coffin 1975, Souci et al. 2000, Santos et al. 2004, Hunt et al. 1991, ATSDR 2005, Reilly 2002, Somer and Unal 2004, De pieri et al. 1996 |
| Vegetables | 40 | 6.4 | 5.43 | 1.73 | 23.3 | 20.8 | |
| Milk and milk products | 22 | 7.32 | 4.7 | 3.1 | 21.2 | 27.6 | |
| Eggs | 15 | 15.2 | 13.8 | 6.87 | 28.5 | 34.5 | |
| Fruits | 29 | 4.67 | 2.9 | 1.09 | 17.4 | 16.6 | |
| Meat and meat products | 29 | 30.9 | 26.9 | 10 | 56.3 | 145 | |
| Offal | 20 | 40.0 | 37.5 | 26.5 | 55.1 | 66.5 | |
| Fish and fish products | 22 | 8.26 | 6.62 | 4.2 | 20.9 | 21.1 | |
| Shellfish | 21 | 25.1 | 21 | 4.2 | 65 | 271 | |

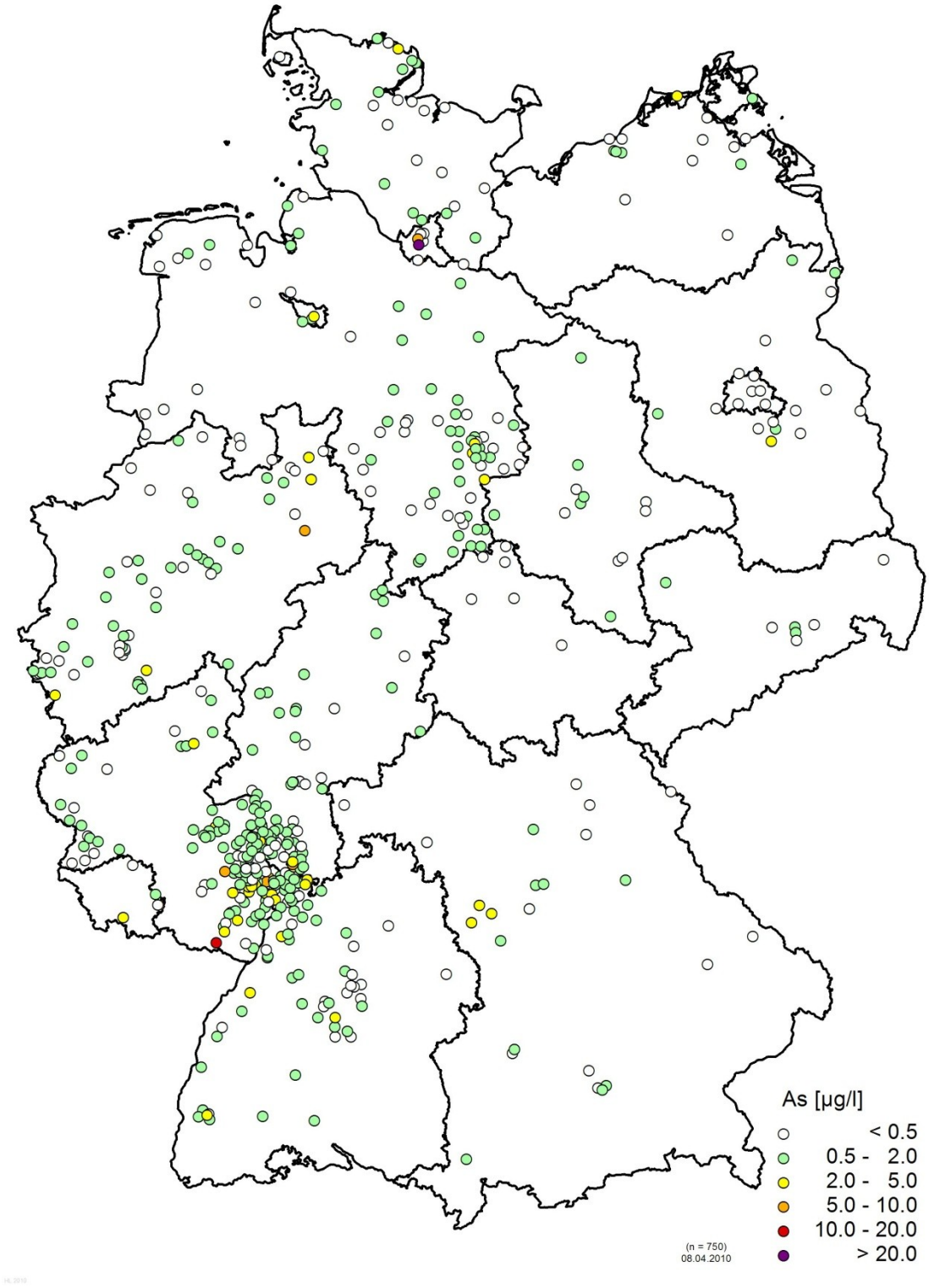


Figure 16 annex: Regional distribution of arsenic in German tap waters

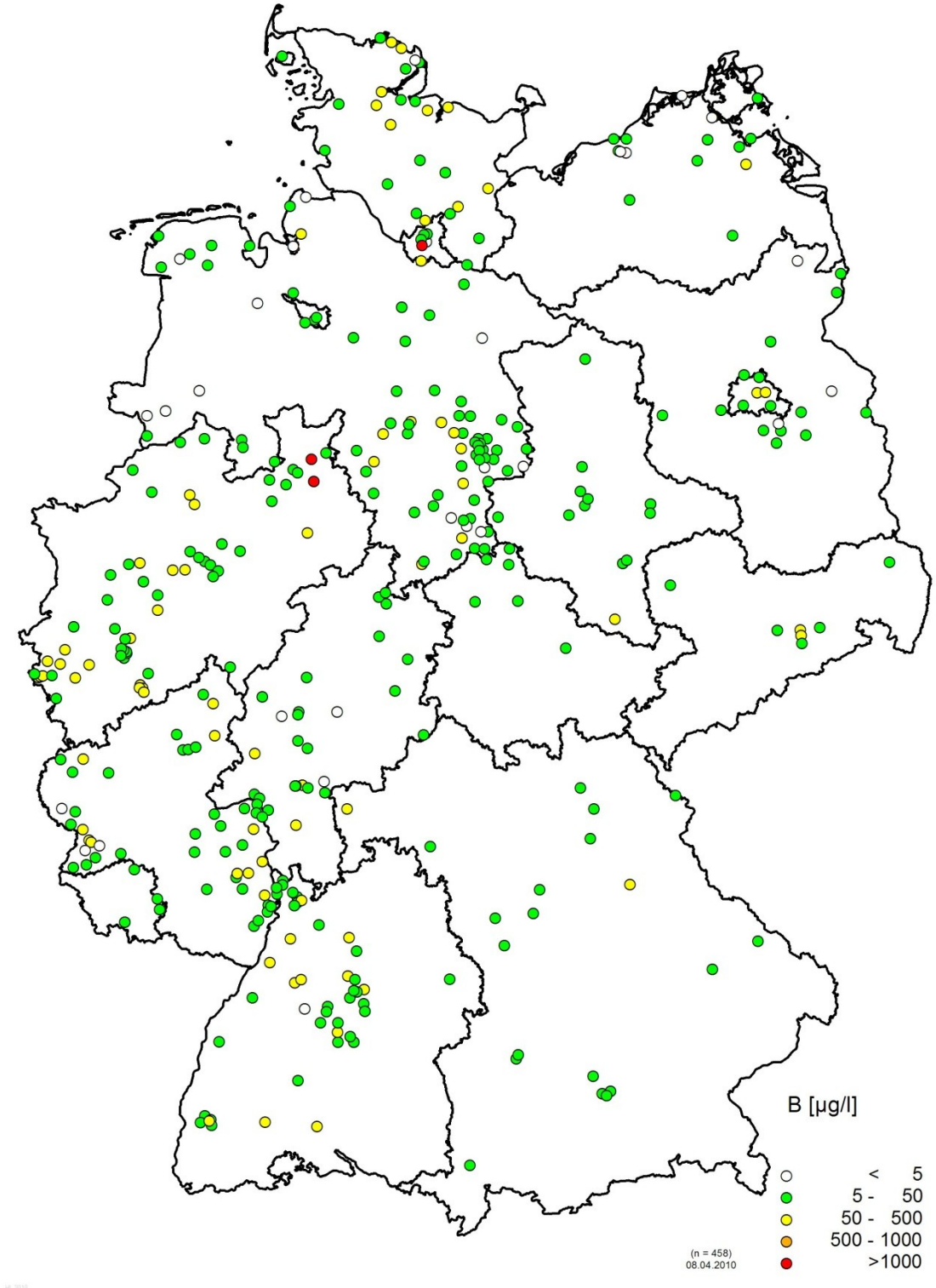


Figure 17 annex: Regional distribution of boron in German tap waters

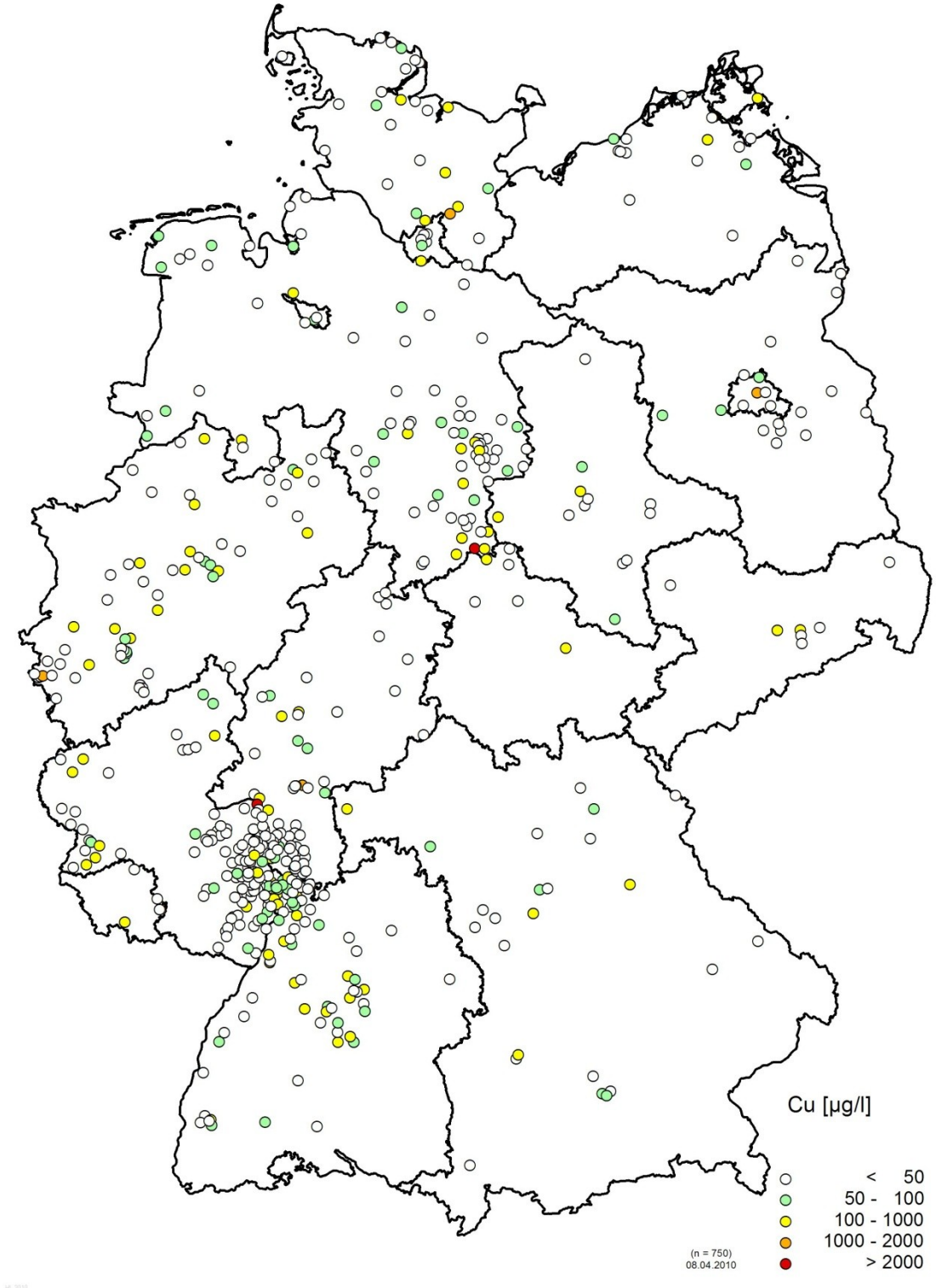


Figure 18 annex: Regional distribution of copper in German tap waters

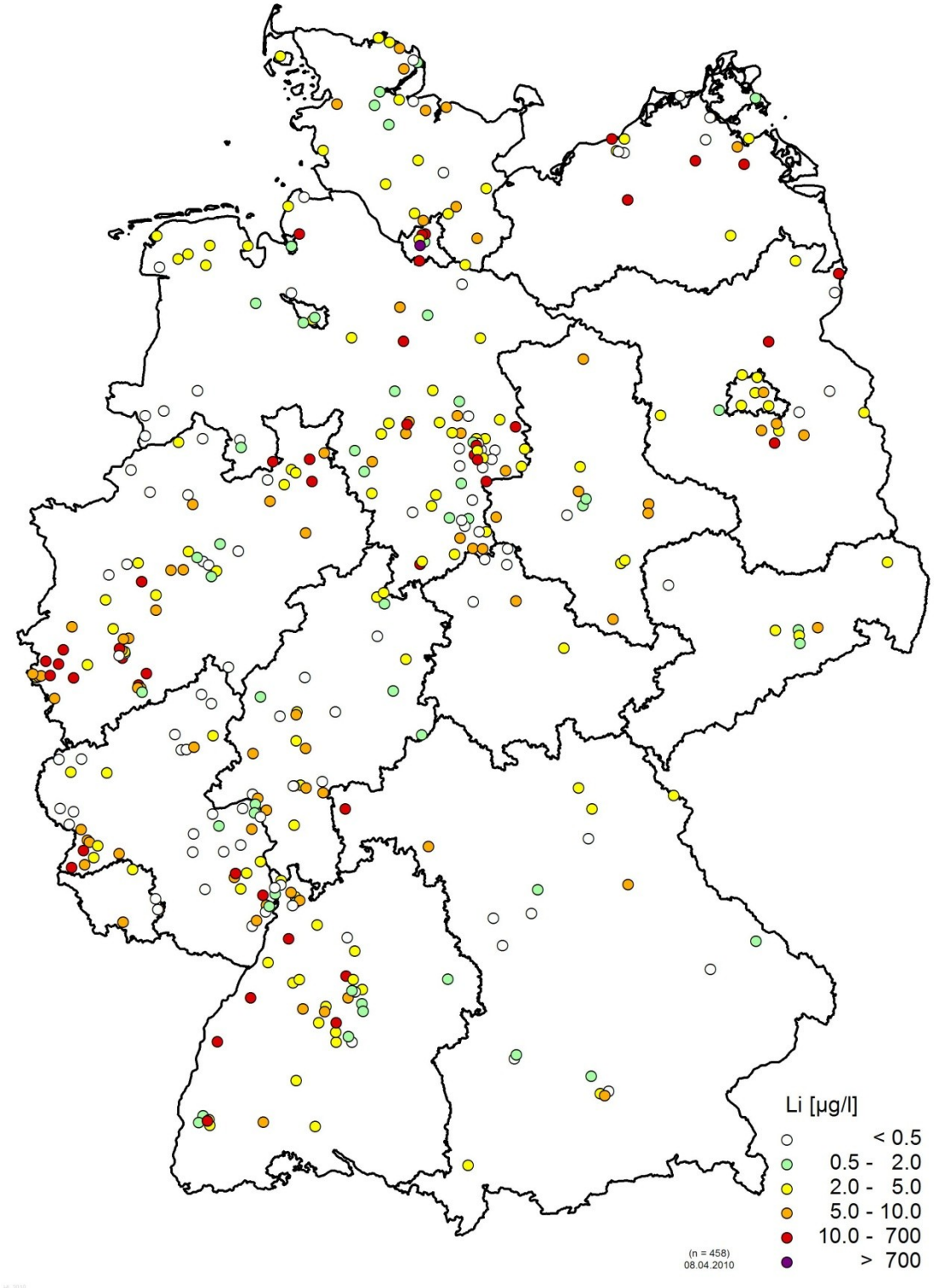


Figure 19 annex: Regional distribution of lithium in German tap waters

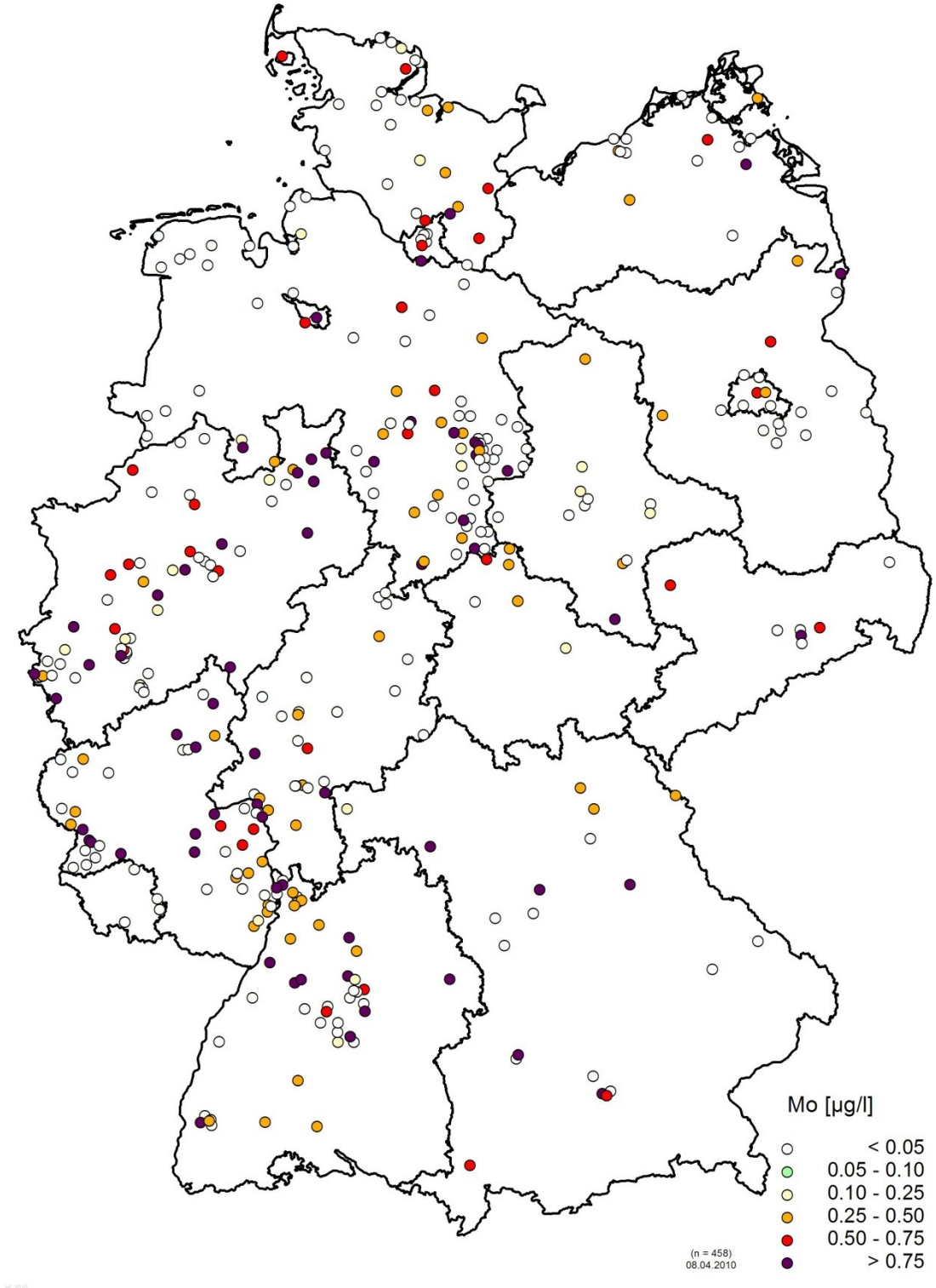


Figure 20 annex: Regional distribution of molybdenum in German tap waters

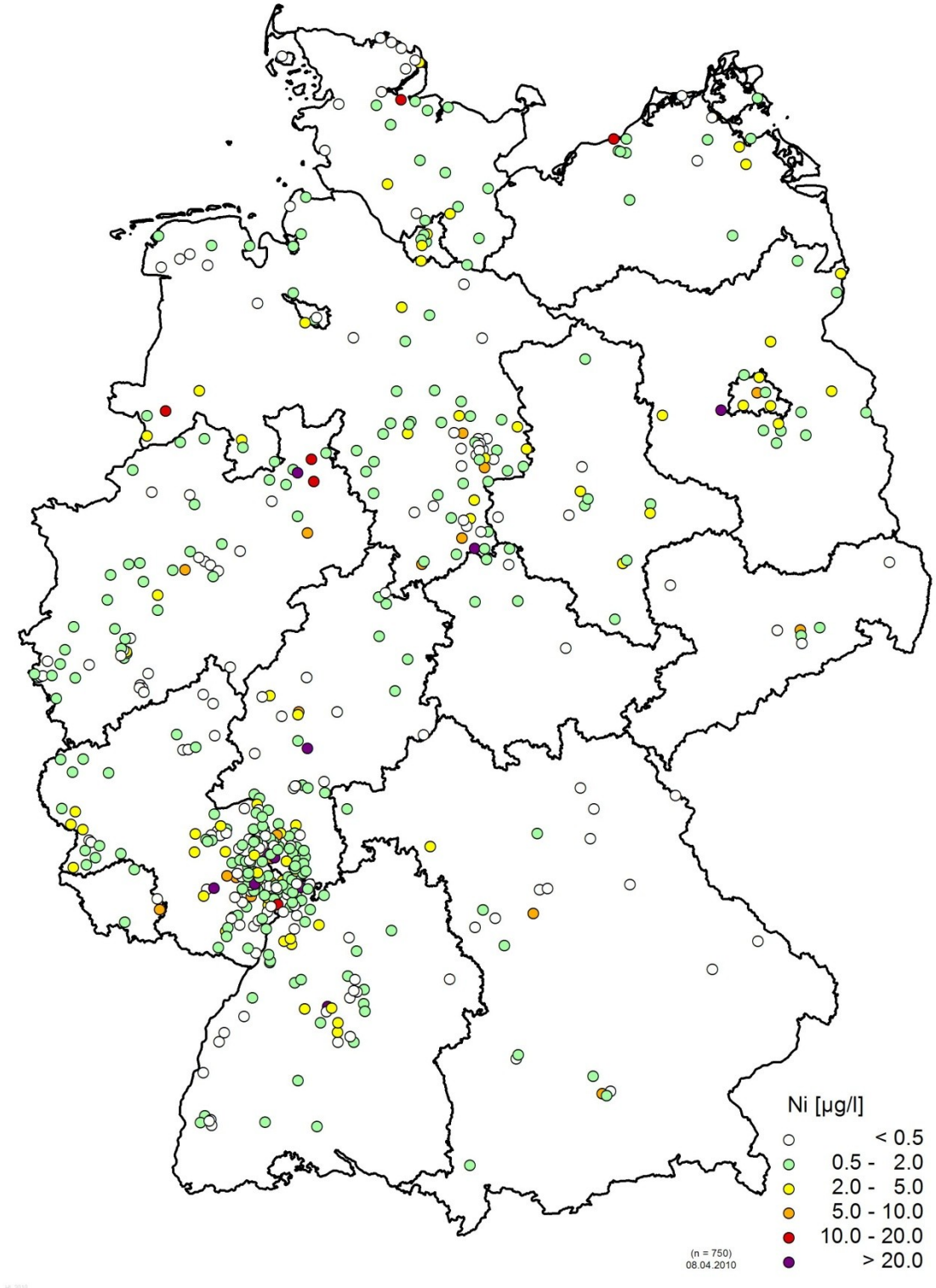


Figure 21 annex: Regional distribution of nickel in German tap waters

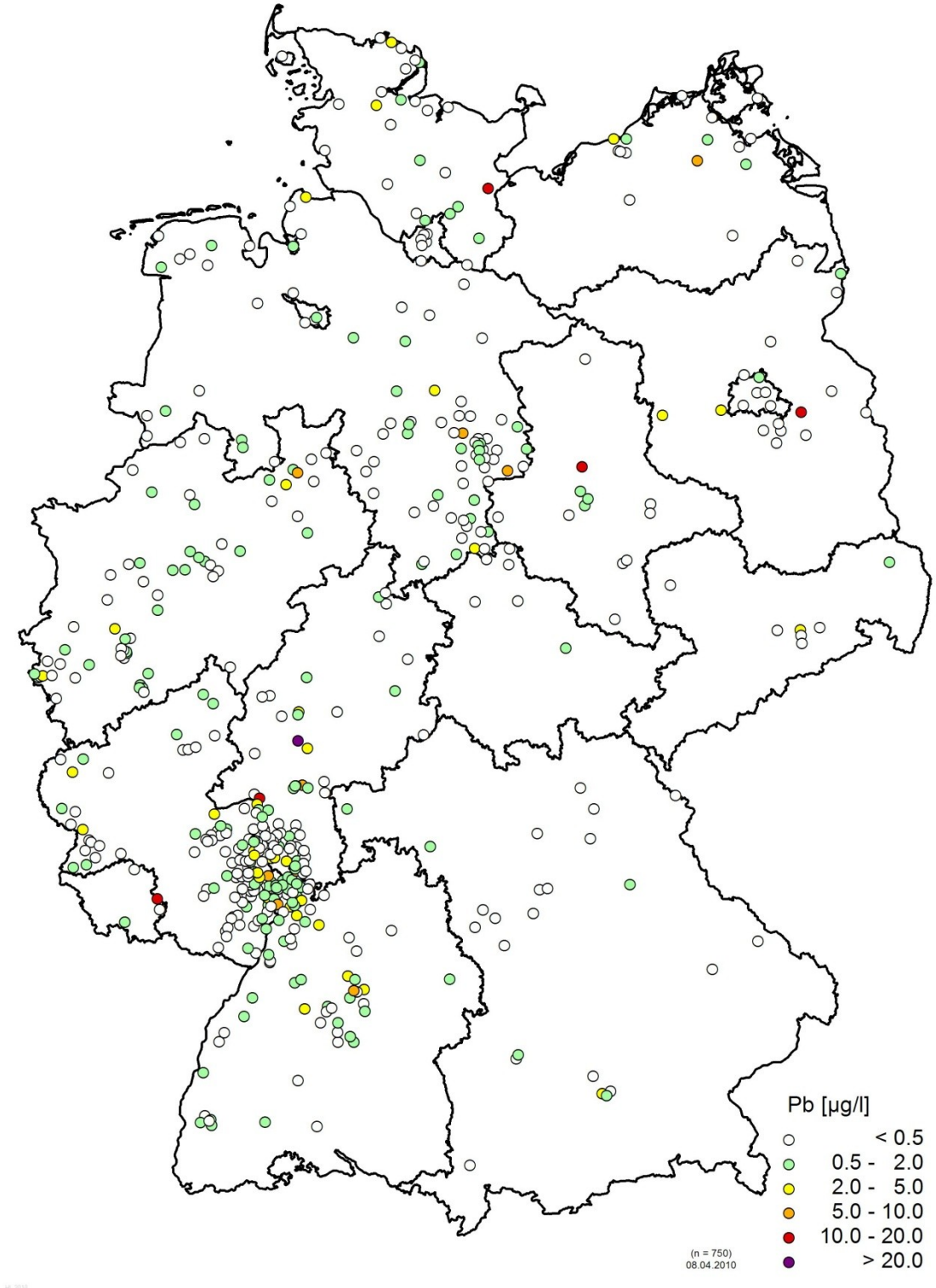


Figure 22 annex: Regional distribution of lead in German tap waters

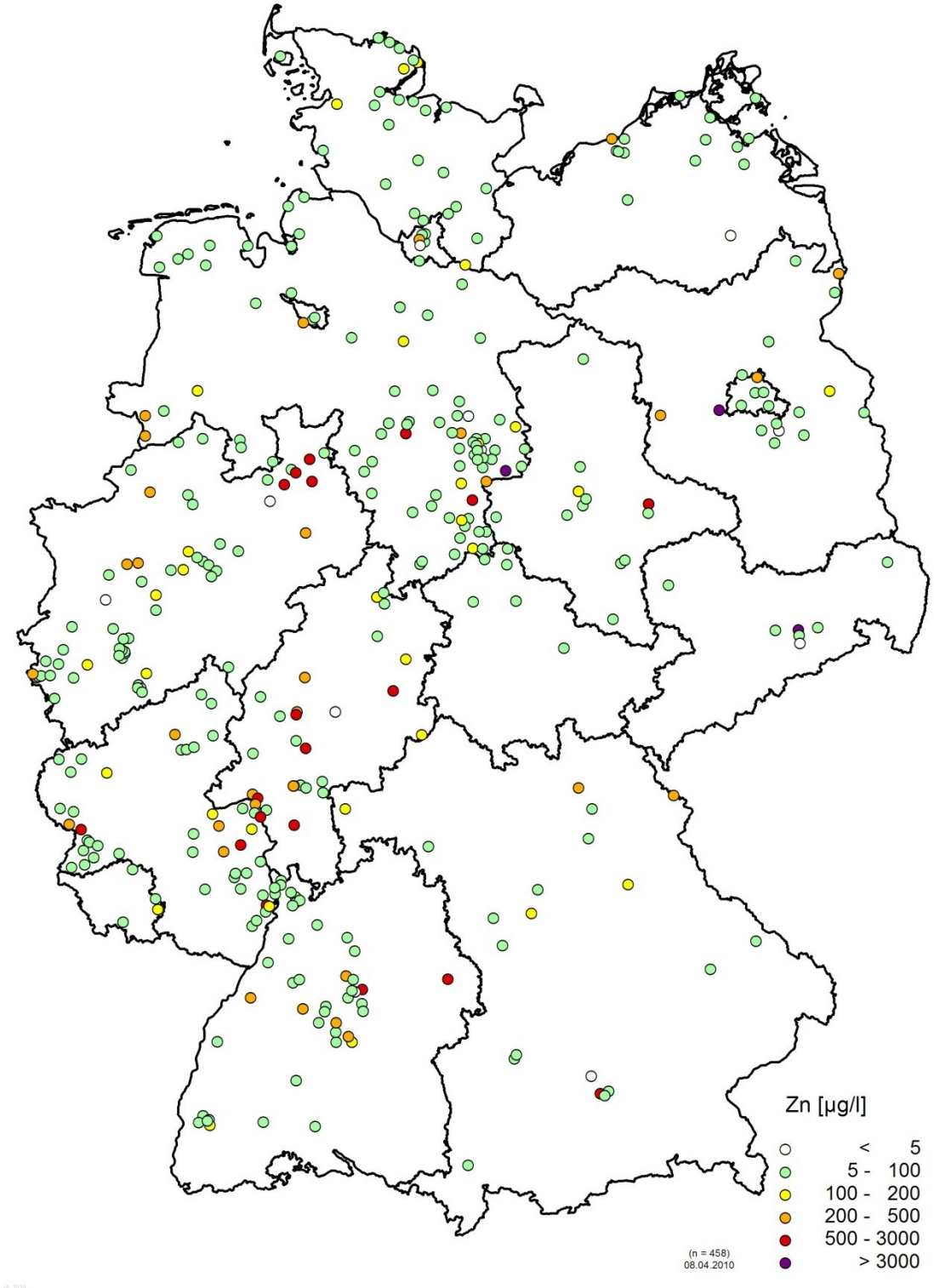


Figure 23 annex: Regional distribution of zinc in German tap waters